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Floodplain Impacts on Water Quality: A Case Study In Southern Louisiana

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FLOODPLAIN IMPACTS ON WATER QUALITY: A CASE STUDY IN SOUTHERN LOUISIANA

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ABSTRACT

The quantity and quality of dissolved carbon delivered to coastal margins by rivers is an important component of global carbon cycling. The Atchafalaya River (AR) discharges ~25% of the flow of the Mississippi River (MR) and the total flow of the Red River (RR) into the Gulf of Mexico (GoM) annually while flowing through the largest bottomland swamp in North America. This provides a unique opportunity to study floodplain impacts on dissolved carbon processes in a large river system. The research aimed to: (1) determine DIC and DOC transport and processing by a river swamp basin under varied seasons and flow conditions, using the AR as a case study; (2) describe how the major tributaries of the AR affect dissolved carbon concentrations and dynamics (3) provide much-needed estimates for export of carbon to the GoM by the AR. From May 2015 -May 2016, I analyzed DOC and DIC concentrations, mass loads, and $\delta\ ^{13}C$ stable isotope composition of waters in the AR's tributaries, and its origin and outlet locations.

The RR contributed the majority of DOC to this system. The MR contributed the majority of DIC. During the study period, the AR exported 5.35 Tg DIC and 2.34 Tg DOC into the GoM. Based on the mass inflow-outflow balance, approximately 0.53 Tg (~10%) of the total DIC exported was produced within the floodplain, while 0.24 Tg (~10%) of DOC entering the basin was removed. All sites were saturated with pCO_2, indicating that this swamp-river system acts a large source of DIC to the atmosphere as well as to coastal margins. Largest downstream changes to concentrations and loads occurred during periods when the adjacent wetlands were deeply inundated. The changes corresponded with shifts in isotopic composition that suggested inputs of DIC from floodplains. This effect was particularly pronounced during early flood

stages. This thesis research demonstrates that a major river with extensive floodplains in its coastal margin can act as an important source of DIC and a sink for DOC.

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CHAPTER 1: INTRODUCTION

1.1 Background

Large rivers play an important role in global carbon cycling, acting not only as conduits of terrestrial carbon from land to sea, but also as active systems for carbon transformation and processing (Butman and Raymond, 2011; Cole et al., 2007). The quantity and quality of end-member carbon exported by rivers to coastal margins has important impacts on marine ecosystem health and functioning, and is important to the development of global carbon budgets (Chavez and Takahashi, 2007; Tank et al., 2013). Studies have shown substantial increases in the global riverine export of terrestrial carbon to oceans over the past several decades, and have linked these increases to human activity such as changes in land use, urbanization, and intensive agriculture (Butman et al., 2015; Evans et al., 2005; Ren et al., 2015). Though carbon export in most major systems has been estimated, many measurement gaps exist due to due to a lack of geographically specific observations of riverine carbon dynamics, leaving global carbon budgets poorly characterized (IPCC 2013).

Riverine dissolved carbon has two primary forms: dissolved organic carbon (DOC), which includes decaying organic material (<0.45 μm) varying greatly in molecular weight and bioavailability, and dissolved inorganic carbon (DIC), which is the sum of inorganic carbon (CO_2, CO_3, HCO_3-, and carbonates of minerals). DIC is derived largely from aerobic respiration (both in runoff from soil and as an in-stream process) and mineral weathering (Hope et al., 1994). Riverine DOC is often mineralized in-stream to produce DIC. DIC can be taken up through photosynthesis to produce new organic matter, or can be lost or gained through atmospheric exchange. River systems have been reported to discharge annually a total of 0.17 to 0.78 Pg DOC (Aitkenhead and McDowell, 2000; Harrisson, et al. 2005; Ludwig et al., 1996;

Mantoura and Woodward, 1983; Meybeck, 1982) and 0.38 to 2.6 Pg DIC into the world's oceans (Cai et al., 2008; Kempe et al., 1991; Lerman et al., 2007; Meybeck, 1982). At the same time, a global net evasion of CO_2 from fluvial sources to the atmosphere has been estimated to range from 0.26 – 1.8 Pg C each year (Aufdenkampe et al., 2011; Cole et al., 2007; Raymond et al., 2013; Regnier et al., 2013; Richey et al., 2002; Tranvik et al., 2009). These large variations of riverine dissolved carbon fluxes demonstrate that, while it has been widely acknowledged that the quality and quantity of end-member carbon exported from rivers to oceans can have profound effects on carbon cycling in coastal ecosystems, many measurement gaps and uncertainties exist in current estimates of carbon exports for many coastal rivers in the world.

The Mississippi-Atchafalaya River System (MARS) is the largest river system in North America, and is among the largest in the world, making its carbon export globally significant (Bianchi et al., 2004, 2007; Raymond and Cole, 2003; Cai et al., 2008). The Mississippi River (MR) drainage basin spans ~41% of the contiguous United States and covers large areas of intensively farmed land, heavily urbanized areas, and population hubs (Goolsby and Battaglin, 2001). Extensive human alteration of this 3,230,000 km² basin has resulted in recent large increases in anthropogenic carbon and nutrient export (Raymond et. al 2008; Turner and Rabalais, 1991). In south-central Louisiana, ~25% of the Mississippi River flow is diverted into the Atchafalaya River (AR), a large (~275 km long) braided river-floodplain system. The AR and the MR together comprise ~90% of freshwater discharge into the Northern Gulf of Mexico (NGOM), andheavily impact estuarine and coastal processes (Meiggs and Taillefert, 2011).

Regions of the NGOM dominated by the Mississippi-Atchafalaya River System (MARS) plume exhibit greatly enhanced productivity as well as disruption of natural biogeochemical cycling (Donner et al., 2004; Lohrenz et al., 1997). Inputs of anthropogenic riverine carbon play

a role in this ecosystem disruption; for example, organic matter exported by the MARS may contribute up to 23% of the O_2 demand necessary for the perpetuation of seasonal severe hypoxic conditions in the Gulf of Mexico (Green et al., 2006; Justic et al., 1997). Though carbon export from the MR has been well studied (eg: Cai, 2003; Cai et al., 2015; Dubois et al., 2010; Leenheer, 1982; Tian et al., 2015), carbon constituents and dynamics in the large and influential AR swamp-river basin remain poorly described.

Though the MARS is often treated as one system, there are many differences between the lower MR and the AR which likely impact the quantity and quality of riverine carbon constituents, necessitating separate analysis of these rivers. While the MR is strictly confined by levees, the AR is highly connected to a large and unconfined floodplain. Floodplain systems can greatly impact aquatic biogeochemical cycling: floodplains have been reported to be effective sinks for riverine nutrients (Lindau et al., 1994; Tockner et al., 1999; Forshay and Stanley, 2005), and have also been shown to heavily influence carbon dynamics (Abril et al., 2014; Briggs et al., 1993; Cai et al., 2016; Teodoru et al., 2015; Tockner et al., 1999). However, it has also been reported that biogeochemical cycling in large rivers is slow due to unfavorable conditions (e.g. Hill, 1979; Alexander et al., 2000). Most DOC, for example, is quickly consumed in headwater streams (Fisher and Likens, 1972), leaving only degraded and recalcitrant remnants in downstream reaches (Wipfli et al., 2007), resulting in C-limitation (Taylor and Townsend, 2010). Large rivers also tend to be supersaturated with CO_2 in respect to the atmosphere (Butman and Raymond, 2011; Cole et al., 2001; Raymond et al., 1997), limiting the possibility for increases in inorganic carbon. It remains unclear whether floodplains in a high-order, anthropogenically degraded system as the MARS would be effective enhancers of the biogeochemical cycling of riverine carbon.

At its formation the diverted portion of the MR is joined by the entire flow of the Red River (RR) and becomes the AR. The fraction of the Atchafalaya River's flow contributed by the RR can vary anywhere from 7% to 70% throughout a given year (Xu and BryantMason, 2011). The waters of the AR therefore display large temporal variations in chemical composition depending on the relative contributions of its tributaries. The RR can dilute the large loads of carbon and nutrients entering the AR and NGOM from the agriculturally dominated and Mississippi River watershed. For example, a study on nitrate in this system concluded that although approximately one-third of the Atchafalaya River's average flow came from the RR, a nearly negligible 3% of the AR's total mass load of nitrate was delivered by the RR (Xu and BryantMason, 2011). The RR also may introduce carbon from different sources which may be more bioavailable. The potential effect of the RR on the MR's anthropogenically enhanced DIC and DOC loads is therefore important when evaluating carbon dynamics in the AR.

The high rates of sediment trapping (Rosen and Xu, 2015; Xu, 2010) and organic nitrogen removal compared to the lower MR (Hupp, 2008; Roberts, 1998; Xu, 2006), demonstrate that there is high connectivity of the AR with its basin. This connectivity could also provide necessary time and space for carbon dynamics and cycling. Annual mass load of organic carbon in the AR decreases from origin to outlet (Shen et al., 2012; Xu, 2013), and end-member dissolved organic matter in the AR is compositionally different from that of the MR (Shen et al., 2012), indicating biogeochemical processing of riverine carbon in the AR system. However, uncertainties remain as to the specific effects of extensive floodplain interactions on instream carbon dynamics in this unique system, and what processes lay behind organic carbon compositional shifts and total mass reduction.

Natural isotopic tracers combined with mass balance data can provide insights into the complex transformations and transport of carbon, and have been successfully used to investigate carbon cycling in stream and riverine systems. Different sources of carbon possess unique $\delta^{13}C$ signatures (Deines, 1980; Ehleringer and Cerling, 2002; Mook et al., 1983; Vogel, 1993). Within aquatic systems, the $\delta^{13}C$ signatures of terrestrially-derived carbon sources are impacted by riverine biogeochemical processes. (Baird et al., 2001; Dubois et al., 2010). Studying isotopic composition of dissolved carbon in the AR may provide useful insight into potential sources and processes responsible for dissolved carbon constituents entering and exiting the Atchafalaya River Basin, reflecting water quality and ecological functioning. Study of DIC and DOC together with $\delta^{13}C$ isotope analysis has not been done in this system, and may provide important insights into whether the AR basin is simply a pipeline for the transport of the MR's carbon loads, or whether these loads change within the basin before being discharged into the NGOM.

1.2 Research Objectives and Hypotheses

This thesis research aimed to investigate a central question of whether a river basin with extensive corridor wetlands, large floodplains, and backwaters can affect dissolved carbon constituents. Specifically, the research was to (1) determine DIC and DOC transport and processing by a river swamp basin under varied seasons and flow regimes, using the Atchafalaya River as a case study; (2) describe how the waters of the AR are compositionally affected, in terms of both quantity and quality of dissolved carbon constituents, by the relative chemical contributions of the RR; and (3) provide much-needed estimates for export of carbon to the NGOM by the AR. The primary goal of the research was to test the hypothesis that floodplain interactions in the Atchafalaya River Basin provide enhanced opportunities for carbon cycling which result in net removal of dissolved organic material and net addition of dissolved inorganic

carbon. Since the mineralization of organic carbon is closely tied to production of dissolved inorganic carbon, studying DIC and DOC concentrations and fluxes together with $\delta^{13}C$ isotopes in the AR may provide new insights into the role of floodplains in riverine carbon processing. If this corridor wetland basin effectively removes riverine organic carbon as well as nutrients and sediment, thorough investigation of how and why this removal occurs may have future management implications for the lower MR, GOM, and other rivers with wide floodplains. Additionally, because this research took place during a 13-month period with abnormally high discharge, results may offerinsight into the response of riverine carbon to climate extremes in light of global climate change.

1.3 Research Approach and Study Area

This research was conducted in the Atchafalaya River Basin (ARB), the largest intact river-swamp system in North America. The ARB was treated as a closed system with the only inflow at its upperbasin location, Simmesport, and outflow at its two lower river basin locations, Morgan City and Wax Lake Outlet. The Atchafalaya River Basin contains a 2,571 km^2 floodway system which is frequently inundated to varying degrees by constant naturally occurring overbank flow (Allen et al., 2008). The majority of overbank flow occurs to the east of the river in the Buffalo Cove and Fordoche subunits, which mimic seasonal water-patterns of the main channel. In contrast, much of the basin to the west of the river (Pat Bay subunit) remains relatively isolated from the flow of the main channel, with the extent of flooding primarily determined by local precipitation (Lambou and Hern, 1983). Unpredictable flooding has excluded human development within the basin, allowing for a rich and diverse mosaic of wetland and bottomland hardwood ecosystems. The AR's discharge is seasonally driven, with flows generally increasing in winter, cresting in late spring or early summer, and diminishing sharply

in late summer and fall (Lambou and Hern, 1983; Xu, 2006). Periods of typical high discharge are associated with the greatest inter-annual variability of discharge (Xu, 2013). Likewise, floodplain inundation can vary dramatically within an year and from year to year, resulting in complex seasonal and spatial variation in water residence times and sediment deposition (Rosen and Xu, 2015).

From May 2015 to May 2016, monthly water samples were collected at the AR's origin and two outlets, as well as in its two large tributaries (the MR and RR). In-situ measurements including river water temperature, dissolved oxygen, and specific conductance were recorded during each sampling event at each location to determine ambient conditions at the time of sampling. The research utilized a mass balance concept combined with isotope techniques. All water samples were analyzed for DIC and DOC concentrations and isotope values ($\delta^{13}C_{DIC}$ and $\delta^{13}C_{DOC}$).

1.4 Synopsis of Chapters

This thesis is divided into two research chapters. In Chapter 2, I compare DIC and DOC concentrations, mass loads, and isotopic composition at the inflow and outflow of the Atchafalaya River over 13 months to examine carbon dynamics as influenced by the AR basin. Chapter 3 examines how the Red River influences riverine dissolved carbon loads in the Atchafalaya River. Chapter 4 summarizes the major findings from the two studies.

CHAPTER 2: FLOODPLAIN IMPACT ON DISSOLVED CARBON CYCLING IN THE MISSISSIPPI-ATCHAFALAYA RIVER SYSTEM

2.1 Introduction

Large rivers play an important role in global carbon cycling, acting not only as conduits of terrestrial carbon from land to sea, but also as active systems for carbon transformation and processing (Butman and Raymond, 2011; Cole et al., 2007). Riverine dissolved carbon has two primary forms: dissolved organic carbon (DOC), which includes decaying organic material (<0.45 μm) varying greatly in molecular weight and bioavailability, and dissolved inorganic carbon (DIC), which is the sum of inorganic carbon (CO_2, CO_3, HCO_3-, and carbonates of minerals) and is derived largely from aerobic respiration (both in runoff from soil and as an in-stream process) and mineral weathering (Hope et al., 1994). Recent studies found that wetlands in tropical floodplains of the central Amazon (Abril et al., 2014) and Zambezi River basin (Teodoru et al., 2015) contributed large inputs of inorganic carbon into river waters, while other studies have demonstrated varying effects of floodplain interactions on DOC (Briggs et al., 1993; Cai et al., 2016; Tockner et al., 1999). It is, however, not known to what degree extensive floodplains in temperate and subtropical regions strongly affect riverine dissolved carbon fluxes.

Riverine DOC is often mineralized in-stream to produce DIC. DIC can be taken up through photosynthesis to produce new organic matter, or can be lost or gained through atmospheric exchange. River systems have been reported to discharge annually a total of 0.17 to 0.78 Pg DOC (Aitkenhead and McDowell, 2000; Harrisson, et al. 2005; Ludwig et al., 1996; Mantoura and Woodward, 1983; Meybeck, 1982) and 0.38 to 2.6 Pg DIC into the world's oceans (Cai et al., 2008; Kempe et al., 1991; Lerman et al., 2007; Meybeck, 1982). At the same time, a global net evasion of CO_2 from all fluvial sources to the atmosphere has been estimated to range from 0.26 – 1.8 Pg C each year (Aufdenkampe et al., 2011; Cole et al., 2007; Raymond et al.,

2013; Regnier et al., 2013; Richey et al., 2002; Tranvik et al., 2009). These large variations of riverine dissolved carbon fluxes demonstrate that, while it has been widely acknowledged that the quality and quantity of end-member carbon exported from rivers to oceans can have profound effects on carbon cycling in coastal ecosystems, many measurement gaps and uncertainties exist in current estimates of carbon exports for many coastal rivers in the world.

The Mississippi-Atchafalaya River System is the largest river system in North America, draining over 3 million km^2 land. Together, these two rivers discharge an annual volume of 673 $km^3\ yr^{-1}$ (MR: 474 km^3, (Joshi and Xu, 2016); AR: 199 km^3, (Rosen and Xu, 2015)) over the past two decades, contributing nearly 90% of the total flow from the continental United States to the Northern Gulf of Mexico (NGOM). Many estimates have been made regarding the quantity of dissolved carbon exported from this system, and these estimates vary largely amongst studies. For instance, estimates for DOC export from the Mississippi River (MR) ranged from 1.51 to 3.48 Tg yr^{-1} (Cai et al., 2015; Dubois et al., 2010; Leenheer, 1982) and for DIC from 13.5 Tg yr^{-1} to 18.8 Tg yr^{-1} (Cai, 2003; Cai et al., 2015; Tian et al., 2015), but these estimates do not account for the portion of the MR diverted through the AR. Estimates for DOC from the Atchafalaya River (AR) fluctuated from 0.76 to 1.33 Tg yr^{-1} (Leenheer, 1982; Shen et al., 2012). Direct sampling for DOC in the AR's main channel (rather than in its bay, where organic matter may undergo rapid change) has not been conducted recently, so characterization of these fluxes in light of increased mobilization of carbon to rivers in recent years (Butman et al., 2014) is critical. Currently, to the best of our knowledge, no report exists concerning DIC export from the AR.

Most organic carbon exported in rivers is allochthonous material that is rapidly consumed in headwater streams (Fisher and Likens, 1972). Once DOC is mineralized in a fluvial environment, byproducts (CO_2 and CH_4) are emitted from surface waters to the atmosphere, so

that remaining DOC in larger, higher order rivers is generally older, less labile, higher molecular weight material (Wipfli et al., 2007). DOC in the Lower Mississippi River is generally highly degraded remnants of organic matter input from its many tributaries. This would lead one to expect that DOC in the lower MR and AR, would remain largely unaltered as it finishes its journey to the NGOM. However, most carbon flux estimates for large rivers, including the Mississippi River, are based on measurements within a confined channel often hundred kilometers upstream of the rivers' mouth, limiting our knowledge of the potential extent of dissolved carbon transformation through natural floodplains in lower river basins and their coastal margins.

The Atchafalaya River carries approximately 25% of the flow of the MR and the total flow of the Red River to the NGOM. The AR is a unique system of high interest because, despite its relatively short length (~225 km), it is the fifth largest river by volume in the North America (Ford and Nyman, 2011). Additionally, it is highly connected to a large and unconfined floodplain, passing through the largest intact freshwater swamp in North America. The AR has been demonstrated to show higher rates of sediment trapping (Rosen and Xu, 2015; Xu, 2010) and organic nitrogen removal than the lower stretch of the MR due to its unique hydrology (Hupp, 2008; Roberts, 1998; Xu, 2006), suggesting that the AR's high connectivity with its basin could also provide necessary time and space for carbon cycling to occur. Annual mass load of organic carbon in the AR has been observed to decrease from origin to outlet (Shen et al., 2012; Xu, 2013), and end-member dissolved organic matter in the AR has been described as compositionally different from that of the MR (Shen et al., 2012), indicating biogeochemical processing of riverine carbon in this system. However, uncertainties remain as to the specific effects of extensive floodplain interactions on instream carbon dynamics in this unique system,

and what processes lay behind observed organic carbon compositional shifts and total mass reduction.

Riverine stable carbon isotope analysis, which describes the ratio of $^{13}C/^{12}C$ in a sample of water, is useful in identifying major sources of dissolved carbon as it interacts with the atmosphere, sediment, and biosphere; isotopic constraining of carbon sources and in-stream processing provides insight regarding the origin and quality of carbon constituents. Carbon derived from the atmosphere, various plant production pathways, and different mineral origins all possess unique $\delta^{13}C$ signatures (Deines, 1980; Ehleringer and Cerling, 2002; Mook et al., 1983; Vogel, 1993). Within aquatic systems, the $\delta^{13}C$ signatures of terrestrially-derived carbon sources are impacted by riverine biogeochemical processes. For example, photosynthesis and atmospheric degassing preferentially remove ^{12}C (Baird et al., 2001) which leaves the remaining aquatic carbon pool enriched in ^{13}C, resulting in a positive shift in $\delta^{13}C$ values; meanwhile respiration processes contribute to ^{13}C uptake, and subsequently more negative isotope values (Dubois et al., 2010). Studying isotopic composition of dissolved carbon in the AR may provide useful insight into potential sources and processes responsible for dissolved carbon constituents entering the Atchafalaya River Basin, reflecting water quality and ecological functioning. Furthermore, downstream changes in $\delta^{13}C$ values would help to indicate floodplain contributions to riverine dissolved carbon cycling.

To better understand the effects of river floodplains on carbon transport, transformation, and retention, we sampled waters and performed in-situ measurements at multiple sites along the Atchafalaya River during a 13-month period, covering a wide range of temperature, flow, and floodplain-river hydraulic connectivity conditions. The study addressed two important questions: 1) how do DIC and DOC concentrations and loads in the AR fluctuate spatially and

seasonally, and 2) what factors and processes are most likely to control this spatiotemporal variability. The primary goal of the study was to test the hypothesis that floodplain interactions in the Atchafalaya River Basin are related to enhanced opportunities for carbon cycling, resulting in a net removal of dissolved organic material and production of inorganic carbon. Since the mineralization of organic carbon is closely tied to production of dissolved inorganic carbon, studying DIC and DOC concentrations and fluxes together with $\delta^{13}C$ isotopes in the AR may provide new insights into the role of floodplains in riverine carbon processing. If this corridor wetland basin effectively removes riverine organic carbon as well as nutrients and sediment, thorough investigation of how and why this removal occurs may have future management implications for the lower MR and GOM. Additionally, this study provides estimates of dissolved carbon fluxes from the AR during a 13-month period with abnormally high discharge, which may offer insight into the response of riverine carbon to climate extremes in light of global climate change.

2.2 Methods

2.2.1 Study Area

Five hundred river kilometers above its outlet to the Gulf of Mexico, a portion of the Mississippi River is diverted into a large distributary. The Old River Control Structure in southern Louisiana controls this process, diverting a federally mandated 30% of the combined flow of the MR and the Red River (RR) to form the AR. The AR travels southwards for ~225 km before entering the NGOM through two outlets: Morgan City and Wax Lake Outlet. The former is a natural channel which delivers approximately 60% of the AR's water to the Gulf, while the latter was constructed in 1942 to redirect the remaining flow away from Morgan City as a flood

control measure. Although the AR is strictly confined by levees in its first 110 km, they later open up to span 35 km across, allowing the river to meander and braid extensively throughout the largest intact wetland forest in North America, spanning 120 km from upstream to downstream. Soils in the basin are a complex amalgamation of soils carried and deposited by the MR and RR from over 30 different states and 2 Canadian provinces, with large amounts of new sediment accretion occurring annually in the basin's abundant low-lying areas with high hydraulic connectivity (Hupp et al., 2008).

The Atchafalaya River Basin (ARB) contains a 2,571 km^2 floodway system which is frequently inundated to varying degrees by naturally occurring overbank flow (Allen et al., 2008). The majority of overbank flow occurs to the east of the river in the Buffalo Cove and Fordoche subunits, which mimic seasonal water-patterns of the main channel. In contrast, much of the basin to the west of the river (Pat Bay subunit) remains relatively isolated from the flow of the main channel, with extent of flooding primarily determined by local precipitation events (Lambou and Hern, 1983). Unpredictable flooding has excluded human development within the basin, allowing for a rich and diverse mosaic of wetland and bottomland hardwood ecosystems. The AR's discharge is seasonally driven, with flows generally increasing in winter, cresting in late spring or early summer, and diminishing sharply in late summer and fall (Lambou and Hern, 1983; Xu, 2006). Periods of typical high discharge are associated with the greatest inter-annual variability of discharge (Xu, 2013). Likewise, floodplain inundation can vary immensely annually and inter-annually, resulting in complex seasonal and spatial variation in water residence times and sediment deposition (Rosen and Xu, 2015).

2.2.2 Water Sampling and Field Measurements

From May of 2015 through May of 2016, 13 sampling events were conducted, taking place at monthly intervals covering a range of flow conditions at three sites along the Atchafalaya River: Simmesport, Wax Lake Outlet, and Morgan City, located, respectively, 7.9 km and 189.4 km (both outlet location) southwest of the ORCS. Prior to reaching Butte la Rose, the AR is strictly confined; after that point, in its last 90 km, the AR is heavily braided and flows through a wide floodplain (Figure 2.1).

During each monthly sampling event, ambient parameters including dissolved oxygen (DO), pH, temperature, and specific conductance were measured and recorded using a YSI 556 multi-probe meter (YSI Inc., Yellow Springs, OH, USA) at each location. Additionally, surface water samples were collected at each site from a depth of 30-50 cm below water surface using an extendable sampler. Although it has been demonstrated that chemical constituents in fast-flowing waters of the AR are uniformly mixed (US Department of Interior, 1969), 3 samples were composited at each location and individual parameters analyzed from this composite. DOC samples were collected in acid-washed, stream-rinsed HDPE bottles. Samples for DIC were placed in 20 mL glass vials without headspace and sealed with PFTE/butyl rubber septa to protect against perturbation and gas exchange, and immediately placed on ice, along with samples to be analyzed for DOC. Duplicate samples were collected at one site per trip for quality control purposes. All samples were stored in coolers with wet ice during transportation; DIC samples were refrigerated until chemical analysis, while DOC samples were filtered and frozen immediately upon return from sampling.

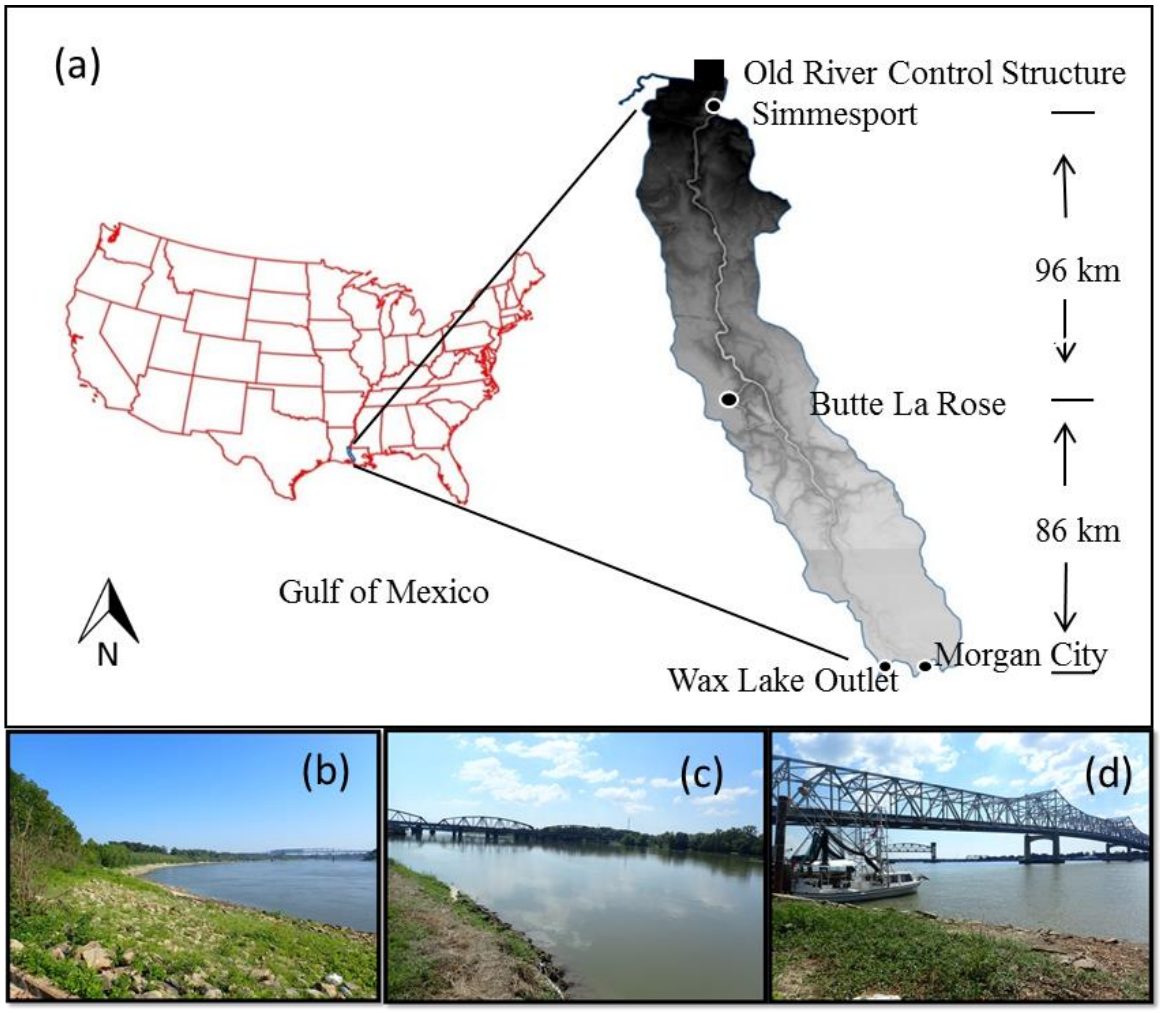

Figure 2.1. (a) Geographical location of the Atchafalaya River entering the Gulf of Mexico. The river carries ~25% of the Mississippi River's water diverted by the Old River Control Structure and the entire flow of the Red River, forming the North America largest river swamp. In this study three sampling sites were chosen for in-situ measurements and water sampling: (b) Simmesport (SIM: 30°58'05.9"N, 91°48'26.2"W), being upstream, and two outlets – (c) Wax Lake Outlet and (d) Morgan City (WLO: 29°42'03.2"N, 91°22'17.6"W ; MOR: 29°41'50.5"N, 91°12'41.9"W) downstream.

2.2.3 Sample Analysis

Upon returning to the lab, samples for DOC were filtered using 0.45 μm nylon syringe filters (Environmental Express, Charleston, SC, USA) and frozen until analysis. DOC and DIC

samples were shipped in insulated coolers filled with blue ice packs overnight to University of California Davis Stable Isotope Facility (http://stableisotopefacility.ucdavis.edu/) for analysis.

DIC samples were analyzed for ^{13}C as well as concentration by trace gas using a GasBench II system interfaced to a Delta V Plus IRMS (Thermo Scientific, Bremen, Germany). Samples were injected into septum capped vials containing 85% phosphoric acid, converting DIC to gaseous CO_2, which was then transferred to an IRMS via a helium carrier stream to determine concentrations and isotopic composition against a set of known standards. Precision of measurements was better than 0.1%.

Filtered DOC samples were analyzed using an O.I. Analytical Model 1030 TOC Analyzer (OI Analytical, College Station, TX, USA) interfaced to a PDZ Europa 20-20 isotope ratio mass spectrometer (Sercon Ltd., Cheshire, UK). Samples are acidified and purged with helium to remove DIC. Samples were reacted with sodium persulfate to convert DOC into CO_2, which was transferred to an IRMS in a helium flow for determination of isotopic composition. Samples are run against potassium hydrogen phthalate references, which are used as a calibration curve, with a precision of measurements better than 0.4%. Error for DOC and DIC concentration calculations was better than 5%.

Stable isotope values are expressed as deviations per mil (‰) from Vienna Pee Dee Belemnite (VPDB), a standard reference material based on the ratio of $^{13}C/^{12}C$ found in a highly ^{13}C-rich belemnite fossil according to the formula:

$$\partial\ 13C\ ‰ = \left(\frac{R_{sample}}{R_{standard}} - 1\right) * 1000$$

where R is the ratio of the numbers (n) of the heavy and light isotope of an carbon ($^{13}C/^{12}C$) in the sample and the reference (Coplen, 2011).

2.2.4 Mass Flux Calculation, pCO_2 Calculation, and Data Analysis

Daily river discharge data from May 1, 2015 to May 31, 2016 from the U.S. Geological Survey (USGS) monitoring stations, namely 07381490 (Simmesport), 07381590 (Wax Lake Outlet), and 07381600 (Morgan City) were obtained from the USGS NWIS website (http://waterdata.usgs.gov/nwis). On days without discharge records due to equipment malfunction, the missing data were filled using a linear interpolation. Mass fluxes of DOC and DIC into and out of the Atchafalaya River Basin were estimated using their concentrations and river discharge at Simmesport (i.e., input) and Morgan City and Wax Lake Outlet (i.e. output) in two ways. First, daily discharge at each site was multiplied by DIC and DOC concentrations measured at corresponding locations in order to determine daily, monthly, and period-total DIC and DOC mass load estimates at each location. For dates between sampling events, DIC and DOC concentrations were assigned as the reported value of the nearest sampling event (e.g., Lambou and Hern, 1983). This approach is based on the assumption that the DIC and DOC concentration measurements are representative for the corresponding month. While this approach is widely used in mass flux calculation for large rivers, certain error exists in the estimation. In order to provide further accountability for estimates, we also calculated mass loading for the period using an additional common method wherein the flow-weighted average concentrations for DOC and DIC at each site were multiplied by corresponding total discharge for the period (e.g., Bianchi et al., 2004). A mass balance of DIC and DOC for the AR basin was established based on their input at Simmesport and combined output at Wax Lake Outlet and Morgan City.

The monthly input-output change in mass is considered as the basin's contribution to dissolved carbon dynamics.

The partial pressure of carbon dioxide in water was calculated according to the method shown by Cai and Wang (1998), which uses DIC concentration and measured pH data in the equation:

$$pCO_2 = \frac{[CO_2]}{K_H} = \frac{C_T\ \{H\}^2}{(\{H\}^2 + \{H\}K_1 + K_1K_2)K_H}$$

where C_T is the measured DIC value, $\{H\} = 10^{-pH}$, K_H is the solubility constant (Weiss, 1974), and K_1 and K_2 are the dissociation constants of carbonic acid. Since sampled waters possessed salinity measurements of less than 0.2, the K_1 and K_2 of Harned and Davis (1943) and Harned and Scholes (1941) were used, respectively, for salinities near 0. K_H, K_1 and K_2 are all adjusted for absolute temperature.

Regression analysis was performed to assess various relationships of DIC and DOC concentrations and fluxes with ambient conditions. Paired t-tests were used to identify downstream changes in chemical constituents from Simmesport to each outlet location using an alpha value of 0.05. Statistical analyses were performed with SAS 9.4 Statistical Software Package (SAS Institute, Cary, NC).

2.3 Results

2.3.1 River Flow and Ambient Conditions

Mean daily discharge at Simmesport reported during this 13-month study (May 1, 2015 to May 31, 2016) was 8,902 (std ± 3,885) $m^3 s^{-1}$, falling as low as 2,166 $m^3 s^{-1}$ in late October and

reaching a maximum rate of 17,443 $m^3 s^{-1}$ in mid-January. Mean daily discharge at Wax Lake Outlet was 3,983 (± 1,572) $m^3 s^{-1}$, ranging from 529 to 6,956 $m^3 s^{-1}$, and mean daily discharge at Morgan City outlet was 4,772 (± 2,112) $m^3 s^{-1}$, fluctuating from 571 to 11,114 $m^3 s^{-1}$. Total water volume passing through Simmesport during the study period was approximately 305 km^3. The inflow was slightly higher than the combined outflow from Wax Lake Outlet and Morgan City (300 km^3). On average (± 2.6%), Wax Lake Outlet and Morgan City distributed 45.5% and 54.5% of the AR's flow into the NGOM, respectively.

Average flow for the 12-month period from May 1, 2015 to April 30, 2015 was 8,854 (± 4,026) $m^3 s^{-1}$, which was about 35% higher than the long-term (1978-2004) annual average (6,547 $m^3 s^{-1}$) reported by Xu (2006), and also exceeded values reported by USGS for water years 2010-2015 which averaged 6,187 $m^3 s^{-1}$ (with yearly averages ranging from 4,967 to 7,229 $m^3 s^{-1}$).

Mean daily discharge rates varied by season. Lowest average daily flows at Simmesport occurred throughout fall (3,126 $m^3 s^{-1}$), followed by summer (10,401 $m^3 s^{-1}$) and spring (10,619 $m^3 s^{-1}$), with highest average daily flow occurring in winter (11,234 $m^3 s^{-1}$). Seasonality of discharge is depicted in Figure 2.2.

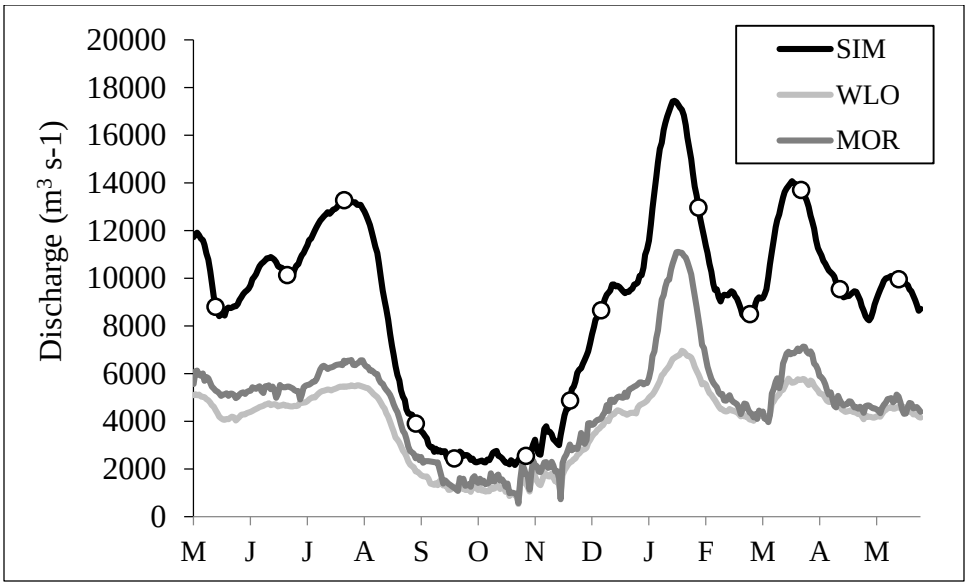

Figure 2.2. Daily discharge at Simmesport (inflow), Wax Lake Outlet (outflow), and Morgan City (outflow) from May 1, 2015 – May 31, 2016 . Markers indicate discharge at Simmesport during each sampling event. Data was obtained from USGS National Water Information System Web Interface (http://waterdata.usgs.gov/nwis).

Average temperature recorded during the sampling trips across all three AR sites was 20.5°C (± 7°C), with individual measurements ranging from 8.1 to 29.9°C during the year. Dissolved oxygen (mg L^{-1}) had a mean value of 7.4 (± 3.1), ranging from 3.3 to 15.6 mg L^{-1}. These two variables showed obvious seasonal trends which mirrored one another (Figure 2.3), and showed strong negative correlation ($R^2 = 0.79$, $p < .001$). pH showed little variation throughout the year (7.7 ± 0.3), with a slight increase from August to October (Table 2.1). No significant differences in ambient conditions were found among sampling sites.

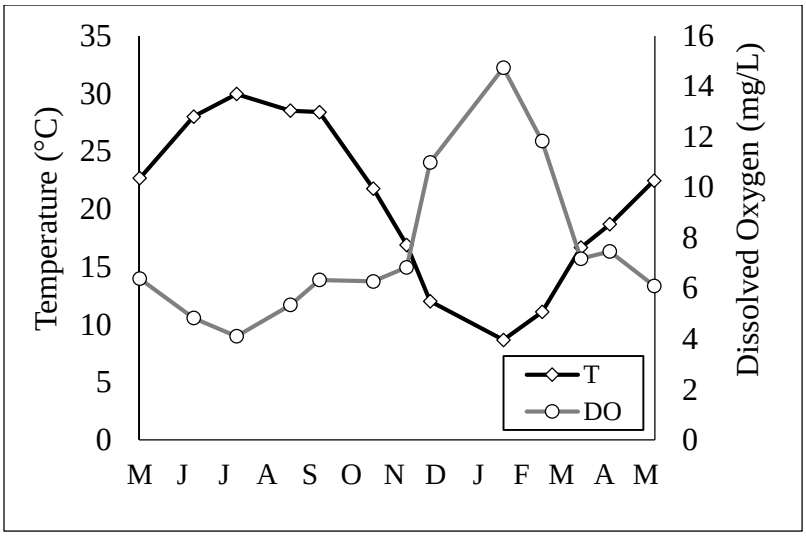

Figure 2.3. Average temperature and dissolved oxygen concentration fluctuations in the AR from May 2015 to May 2016.

Table 2.1. Ambient water quality conditions at Simmesport (SIM), Wax Lake Outlet (WLO), and Morgan City (MOR) for each sampling event.

Sampling Date	Simmesport			Wax Lake Outlet			Morgan City Outlet		
	T (°C)	pH	DO (%)	T (°C)	pH	DO (%)	T (°C)	pH	DO (%)
5/13/2015	22.5	7.3	78.7	22.7	7.3	71.4	23.2	7.5	70.4
6/21/2015	27.6	7.2	63.4	28.2	7.5	65.3	28.4	7.3	52.0
7/22/2015	29.8	7.6	59.1	29.9	7.7	53.5	30.3	7.5	44.2
8/30/2015	28.3	7.9	77.8	28.6	8.1	63.5	28.8	7.7	62.5
9/20/2015	28.1	8.2	82.7	28.1	8.1	69.0	28.2	8.1	77.9
10/29/2015	21.1	7.5	71.5	21.6	8.3	69.5	21.7	8.0	67.9
11/22/2015	16.5	7.4	73.1	17.2	7.7	71.9	17.0	7.6	67.7
12/9/2015	11.6	8.0	102.2	12.2	7.5	90.7	12.6	8.0	103.2
1/31/2016	8.6	7.8	128.7	8.1	7.9	132.6	10.5	7.5	124.4
2/28/2016	10.4	7.5	96.7	12.0	7.7	119.9	11.3	7.9	89.7
3/27/2016	16.9	6.2	75.1	16.9	6.1	73.8	17.5	6.2	66.9
4/17/2016	18.3	6.9	79.3	18.9	7.1	86.6	19.3	7.1	74.7
5/19/2016	22.1	7.6	67.7	22.8	7.5	68.5			
Mean	20.1	7.5	81.2	20.6	7.6	79.7	20.7	7.5	75.1

2.3.2 Dissolved Inorganic Carbon Concentrations, pCO_2, and $\delta\ ^{13}C_{DIC}$

DIC concentrations in the Atchafalaya River's main stem (with all sites included) averaged 1579 (± 521) μmol L^{-1} during the sampling period. All sites showed the same seasonal trend of peak concentrations in late summer and fall, and steady decrease before rising again in late spring (Table 2.2). This pattern demonstrates the negative correlation between DIC concentrations and riverine discharge, with dilution during spring and winter floods, and higher concentrations during low flow. Across all sites, concentrations were on average lowest in March 2016, with a mean value of 773 μmol L^{-1}, and highest in September 2015, with mean value of 2432 μmol L^{-1}. Individual measurements ranged from 672 to 2706 μmol L^{-1}.

Table 2.2. DIC concentrations (μmol L^{-1}) and $\delta\ ^{13}C_{DIC}$ (‰ VPDB) at Simmesport, Wax Lake Outlet, and Morgan City during each sampling event.

Sampling Event	Simmesport		Wax Lake Outlet		Morgan City Outlet	
	DIC	$\delta\ ^{13}C_{DIC}$	DIC	$\delta\ ^{13}C_{DIC}$	DIC	$\delta\ ^{13}C_{DIC}$
5/13/2015	1289	-13.12	1480	-13.20	1485	-13.37
6/21/2015	1510	-14.58	1719	-13.85	1763	-14.26
7/22/2015	1730	-14.11	1884	-13.89	1898	-14.55
8/30/2015	2706	-11.56	2232	-11.12	2294	-12.51
9/20/2015	2508	-10.06	2416	-10.26	2372	-10.13
10/29/2015	1580	-12.19	2258	-12.05	2286	-12.10
11/22/2015	1107	-14.16	1283	-14.06	1297	-13.74
12/9/2015	972	-14.78	1326	-12.95	1497	-13.47
1/31/2016	n/a	n/a	n/a	n/a	n/a	n/a
2/28/2016	1428	-13.18	1366	-13.61	1307	-13.26
3/27/2016	672	-14.86	811	-14.37	835	-14.96
4/17/2016	1118	-16.19	1203	-15.54	1147	-15.60
5/19/2016	1239	-14.65	1264	-13.99	1317	-14.55
Mean	1488	-13.62	1604	-13.24	1625	-13.54

DIC concentrations in the Atchafalaya River's main stem tended to increase from origin to outlets (Table 2.2). However, changes in concentration were not found to be statistically significant ($\alpha = 0.05$) between Simmesport and Wax Lake ($p = 0.17$, $t = -1.46$) or between Simmesport and Morgan City ($p = 0.13$, $t = 1.61$). Flow-weighted average DIC concentrations (reported in μmol L^{-1} with) at Simmesport, Wax Lake Outlet, and Morgan City were 1175, 1291, and 1284, respectively. Downstream increases were especially apparent in October and December. Only samples collected in August, September, and February showed slight decreases in DIC concentrations downstream.

Throughout the sampling period, all sites exhibited CO_2 supersaturation withrespect to atmospheric CO_2 pressure (Figure 2.4). Calculated pCO_2 ranged from 551 μatm to 6,922 μatm. pCO_2 did not show the same seasonal trend as DIC concentrations, with highest values calculated in spring and summer months (particularly June 2015 and April 2016), and lower values more closely resembling atmospheric pressure throughout fall and winter. Spatially, pCO_2 showed no statistically significant change from Simmesport to downstream locations at Wax Lake Outlet ($p = 0.16$, $t = 1.52$) or Morgan City ($p = 0.27$, $t = 1.19$). pCO_2 had no relationship with DIC concentrations ($R^2 = 0.08$, $p = 0.12$)., it showed a strong negative correlation with $\delta\ ^{13}C_{DIC}$ ($R^2 = 0.34$, $p < 0.001$).

$\delta\ ^{13}C_{DIC}$ (‰ VPBD) values followed a seasonal trend similar to that of DIC concentrations at all sites, with more positive values occurring in late summer and fall, and increasingly negative values throughout winter (Table 2.2). Values ranged from -16.19 ‰ in April 2016 to -10.06 ‰ in October 2015. $\delta\ ^{13}C_{DIC}$ values showed a significant positive shift from Simmesport to Wax Lake Outlet ($p = 0.04$, $t = 2.26$), but did not change significantly from Simmesport to the AR's outlet at Morgan City ($p = 0.63$, $t = 0.49$). Downstream changes were

observed from winter through late summer (particularly in December), but little change was observed at downstream locations in fall months. $\delta\ ^{13}C_{DIC}$ values showed a strong positive correlation with DIC concentrations ($R^2 = 0.64$, $p < .0001$), as well as a strong negative correlation with discharge at Simmesport ($R^2 = 0.57$, $p < .0001$)

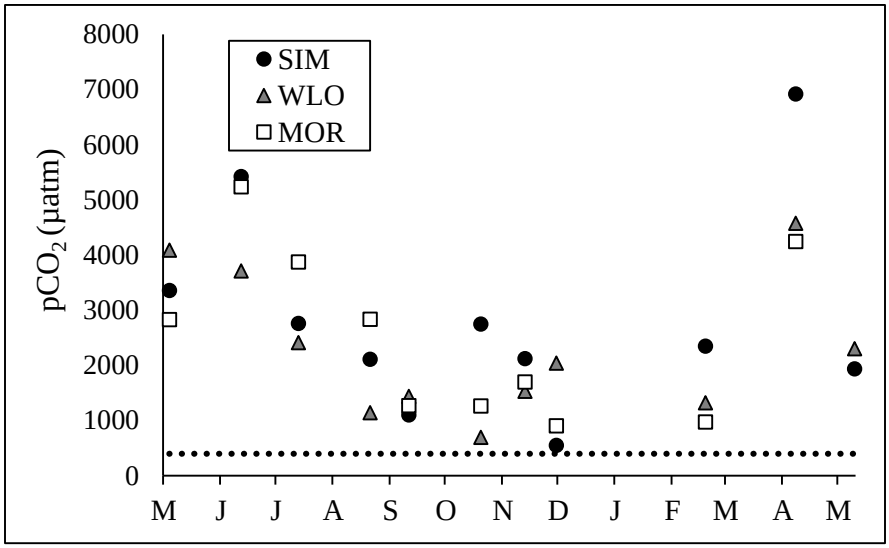

Figure 2.4 Calculated pCO_2 in the Atchafalaya River at its origin (SIM) and two outlets (WLO, MOR) calculated for sampling dates from May 2015 to May 2016 (no calculation is available for the sampling events on 1/31/2016 or 3/27/2016)

2.3.3 Dissolved Organic Carbon Concentrations and $\delta\ ^{13}C_{DOC}$

DOC concentrations in the AR were consistently lower than DIC concentrations. Concentrations of DIC were double those of DOC on average, and were five times higher than DOC in September and October. DIC:DOC ratios (Figure 2.5) tended to increase with increases in temperature and decreased with discharge ($R^2 = 0.28$, $p = 0.002$; $R^2 = 0.40$, $p < 0.001$). Over all sampling events and sites, DOC concentrations averaged 674 (± 218) µmol L^{-1}. Mean DOC was lowest in warm summer months, peaked in the fall, and remained relatively high throughout cool months. Lowest concentrations were reported in October 2015 with a mean value of 281

μmol L^{-1}, and highest concentrations were reported in November 2015 with a mean value of 1069 μmol L^{-1}. Individual measurements ranged widely from 263 to 1172 μmol L^{-1} (site-specific DIC and DOC concentrations for each sampling event are shown in Tables 2.2 and 2.3).

DOC concentrations did not show a strong or consistent longitudinal trend ($f = 0.42$, $p = 0.74$), but tended to decrease from the river's inflow to its outflow. Flow-weighted average DOC concentrations (μmol L^{-1}) at Simmesport, Wax Lake Outlet, and Morgan City were 745, 724, and 669, respectively. Generally, downstream changes in DOC concentration were slight compared to changes in DIC concentration. DIC:DOC ratios increased from origin to outlet in 9 of 12 sampling events, most notably in October (Figure 2.5).

Table 2.3. DOC concentrations (μmol L^{-1}) and $\delta\ ^{13}C_{DOC}$ (‰ VPDB) at Simmesport, Wax Lake Outlet, and Morgan City during each sampling event

Sampling Event	Simmesport		Wax Lake Outlet		Morgan City Outlet	
	DOC	$\delta\ ^{13}C_{DOC}$	DOC	$\delta\ ^{13}C_{DOC}$	DOC	$\delta\ ^{13}C_{DOC}$
5/13/2015	508	-27.67	786	-28.98	384	-26.76
6/21/2015	738	-28.43	601	-27.81	720	-28.10
7/22/2015	519	-27.68	548	-27.81	548	-27.93
8/30/2015	358	-28.15	511	-28.33	496	-28.02
9/20/2015	515	-28.79	522	-28.25	442	-29.41
10/29/2015	309	-27.67	270	-27.12	263	-26.99
11/22/2015	1111	-27.43	1172	-27.62	925	-27.67
12/9/2015	847	-27.78	828	-28.54	788	-28.59
1/31/2016	1087	-28.91	807	-28.34	810	-28.15
2/28/2016	635	-27.85	766	-27.90	743	-28.48
3/27/2016	949	-28.77	814	-28.85	724	-28.47
4/17/2016	731	-28.15	759	-28.08	712	-27.90
5/19/2016	692	-27.90	679	-28.16	687	-28.21
Mean	692	-28.09	697	-28.14	634	-28.05

$\delta\ ^{13}C_{DOC}$ (‰ VPBD) values showed little variation, ranging from -28.98 ‰ to -26.76 ‰ and showed no identifiable spatial or seasonal trend, nor any relationship to DOC concentrations

(R^2 = 0.09, p = .06). There were no significant changes observed in $\delta\ ^{13}C_{DOC}$ values from Simmesport to downstream locations at Wax Lake Outlet (p = 0.76, t = 0.30) or the AR's outlet at Morgan City (p = 0.80, t = 0.25). $\delta\ ^{13}C_{DOC}$ values were unrelated to any measured parameter.

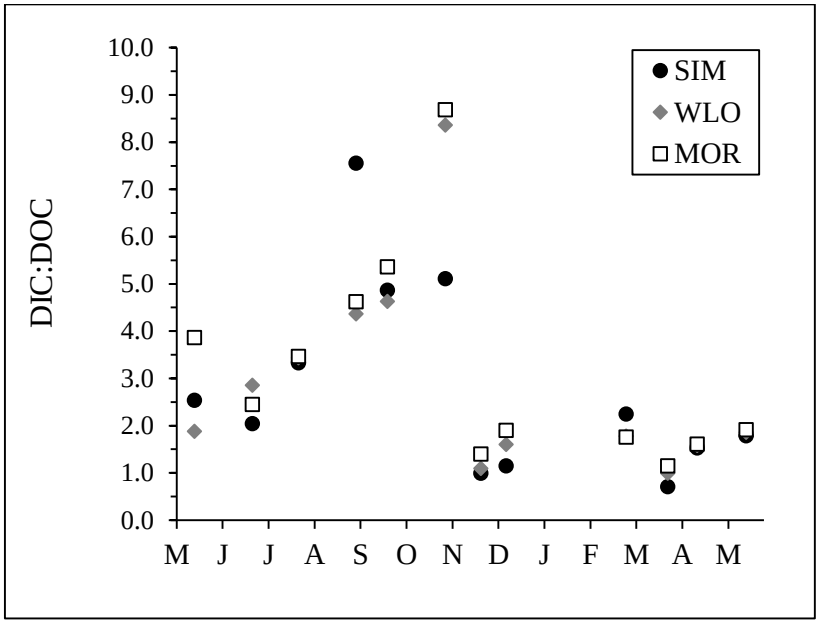

Figure 2.5. DIC:DOC concentration ratios in the Atchafalaya River at its origin (Simmesport) and two outlets (Wax Lake Outlet, Morgan City) observed on 12 monthly sampling dates from May 2015 to May 2016 (no ratio is available for the sampling event on 1/31/2016).

2.3.4 DIC and DOC Mass Flux and Mass Balance

Over the 13-month sampling period, the Atchafalaya delivered an estimated 5.346 Tg DIC and 2.473 Tg DOC into the NGOM. Both dissolved carbon species showed seasonal mass loading trends that closely followed the AR's hydrograph, with lowest export throughout the fall during low discharge, and peak export during high discharge in January. DOC and DIC mass export both showed peaks during winter flooding, but in summer months, DIC mass load increases were more pronounced than DOC (Figure 2.6).

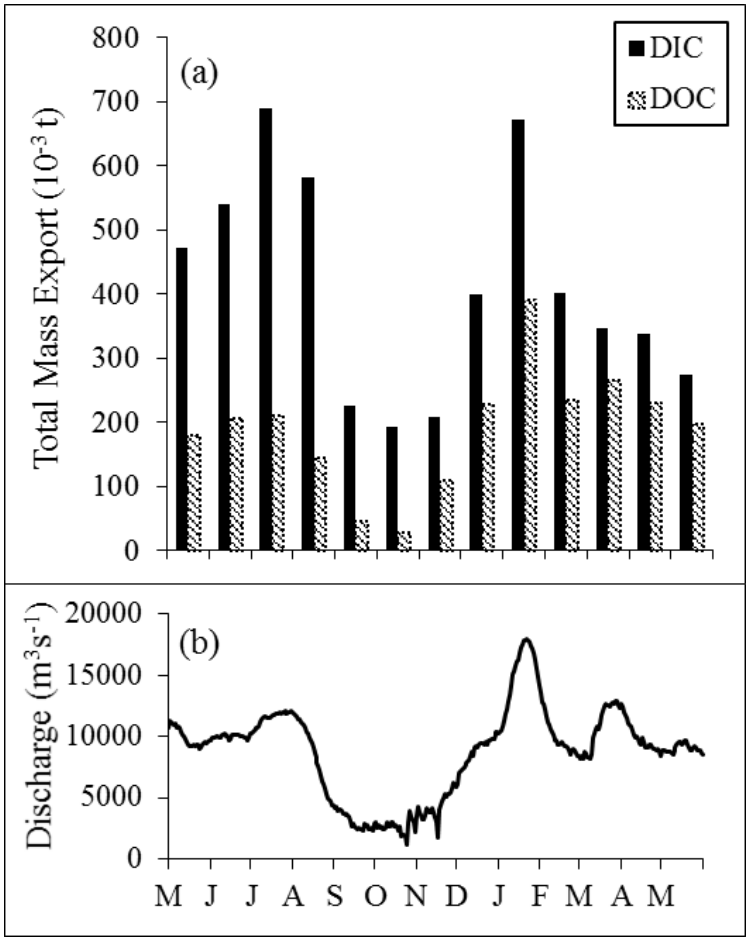

Figure 2.6. a) Monthly mass export of DOC and DIC from the Atchafalaya River's two outlets, Wax Lake outlet and Morgan City, into the Gulf of Mexico during the period of May 2015 to May 2016. b) Daily water discharge from the Atchafalaya's combined outlets into the Gulf of Mexico during the study period.

Over the entire sampling periodan estimated 0.524 Tg of the total DIC discharged into the NGOM was produced within the Atchafalaya basin, and 0.243 Tg of the total DOC entering the basin was retained (Table 2.4). DIC mass load showed a net increase from origin to outlets in all but two months (February - March). DIC instream load increase was notably smallest from mid-summer to early fall, with largest mass load increases at the outflow occurring in December and January. Conversely, DOC mass load decreased from origin to outlets most months, with slight increases observed in May, and August – October (Figure 2.7).

In order to provide further accountability for these estimates, we also calculated mass loading of DIC and DOC for this study period using the flow-weighted average concentrations at each site and their respective average discharges. This secondary method estimated that 4.644 Tg DIC and 2.504 Tg DOC were discharged into the NGOM by the AR's combined outlets. This method estimated that 0.076 Tg of the DOC entering the AR at Simmesport was retained by the basin, while 0.572 Tg of DIC were produced within the basin. Both methods agree that the AR acted as a sink for DOC, and a source for DIC. This method may be less accurate since it cannot account for relationships between concentrations and discharge.

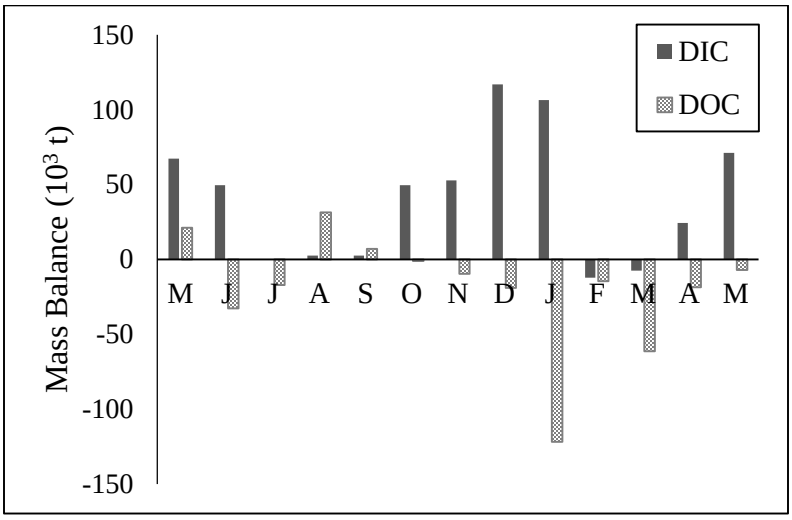

Figure 2.7. DIC and DOC monthly mass balance in the AR (Mass Balance = monthly export from outlets – monthly export at Simmesport). Positive values indicate mass load increase from inlet to outlet.

2.4 Discussion

The results of this study indicate that the Atchafalaya River acts as a significant source for dissolved inorganic carbon, both to coastal margins and to the atmosphere, as well as a potential sink for dissolved organic carbon. Throughout the study period, calculated mass loads of DIC increased significantly ($p < 0.01$) from the AR's origin to its combined outlets (Figure

2.7). Though not statistically significant at the $\alpha = .05$ level, our findings also showed consistent increases in DIC concentrations from inlet to outlets, as well as increases in pCO2, and significant changes in $\delta\ ^{13}C_{DIC}$ values. Many factors may have contributed to this increase, but without additional research it is not possible to separate them. However, based on the strong seasonal signal, we draw several very likely inferences. First, we suggest that strong heterotrophy in the system was responsible for some portion of the observed increase in DIC concentration from origin to outlet during summer months. Second, we suggest that during periods of extensive floodplain inundation, the Atchafalaya's waters come into contact with large amounts of DIC stored in the river's floodplains as byproducts of soil and root respiration, the mineralization of labile organic matter within the basin, and direct inputs of CO_2 into the water column by wetland vascular plants, greatly increasing DIC mass loads at outlet locations.

2.4.1 Dissolved Inorganic Carbon Dynamics

The mineralization of organic matter to DIC through aerobic respiration may play a major role in in-stream DIC increase in this system (Hope et al., 1994). In-stream primary production in summer months can lead to a strong heterotrophic response in riverine systems, where respiration rates outpace the rate of photosynthesis (Cole et al., 2001; Gupta et al., 2008; Khadka et al., 2014; Wang and Veizer, 2000). Respiration rates have been observed to be highest in the AR delta in summer months, corresponding with highest rates of nutrient uptake for primary production (Roberts and Doty, 2015). This is likely also the case for the AR's upstream floodplain ecosystems and main stem. The consistent and significant mass load increases in DIC from origin to outlet found throughout this study (Figure 2.7.) might reflect that high productivity in this nutrient rich, subtropical basin leads to a strong heterotrophic response,

rapidly mineralizing organic material and subsequently causing DIC to accumulate as waters flow through these floodplains.

Concentrations and total mass export of DIC from this system into the NGOM were both found to be generally highest in summer and early fall months (especially June - August: Table 2.2; Figure 2.6), but downstream increases of DIC within the basin were small during a large portion of the same period (July-September) (Figure 2.7). Concentrations even showed an uncharacteristic decrease from origin to both outlets in August and September. This lack of in-stream increase may seem counterintuitive if respiration rates (and thus, production of DIC) are highest in warm productive months. However, outgassing of aqueous carbon dioxide to the atmosphere, which is known to occur in most rivers, particularly during highly saturated summer months when the pressure gradient between aqueous and atmospheric CO_2 is large, (Butman and Raymond, 2011; Cole et al., 2001; Raymond et al., 1997), may provide an explanation. Calculations for this study period show that the AR was supersaturated with CO_2, particularly in spring and summer months (Figure 2.4). This degree of supersaturation would lead to rapid degassing of CO_2 to the atmosphere co-occurring with DIC production (Butman and Raymond 2011; Gupta et al., 2008), resulting in little net change in DIC concentrations and mass loads downstream. The positive shift in $\delta\ ^{13}C_{DIC}$ values from August through October (Table 2.2) could also provide evidence of high rates of degassing simultaneous with DIC production. During CO_2 evasion, the lighter ^{12}C isotope is preferentially outgassed, leaving the resulting aqueous carbon pool enriched in ^{13}C (thus, less negative values for $\delta\ ^{13}C_{DIC}$) (ie., Geldern et al., 2014) .

Although net heterotrophy is indicated in the AR, heterotrophy in main channels normally can only account for less than 20% of CO_2 outgassing flux (Devol et al., 1995; Ellis et al., 2012). Other carbon sources from within the AR's floodplains must then contribute

significant amounts of dissolved carbon to the AR's main channel. For example, October showed the greatest change in DIC concentrations, which increased by > 42% at both outlet locations while DOC concentrations were reduced at both outlet locations by only > 12%. Direct mineralization of riverine DOC to DIC cannot then be the only cause of DIC increase. Despite increasing DIC concentrations downstream, there was a large reduction in riverine pCO_2 from 2748 µatm at Simmesport to 697 µatm and 1268 µatm at Wax Lake and Morgan City outlets, respectively. Thus, CO_2 was lost to the atmosphere without rapid replacement by respiration as was seen in summer months. Although some mineralization of DOC to DIC likely took place, a more appropriate explanation for these increases in DIC concentrations downstream may be the increased influence of carbon weathering in local soils on DIC concentrations during low-flow periods, wherein floodplain contributions to riverine DIC concentration do not become heavily diluted. A recent study comparing three rivers in France found that water pCO_2 was strongly influenced by local soil pCO_2, and that lower water pCO_2 along a watercourse was caused by lower inputs of soil pCO_2 downstream rather than a decrease in degassing (Polsenaere and Abril, 2012). The same study found that a less negative $\delta^{13}C_{DIC}$ signature might occur despite a relatively weak water-air pCO_2 gradient due not largely to degassing, but rather the contribution of carbonate weathering, which has a $\delta\ ^{13}C$ isotopic signature of 0‰ (Mook et al., 1983). From August through October, the AR experienced low flow conditions, heightened DIC concentrations, a relatively weaker water-air pCO_2 gradient, and less negative $\delta^{13}C_{DIC}$ values. This combination of factors suggests that the AR's floodplain soils act as a source of DIC to the AR's waters.

Carbon dioxide stored in soils is often a result of root respiration and microbial oxidation of soil organic matter (Cerling et al., 1991; Coleman, 1973). Evidence suggests that in a

floodplain swamp, up to half of the CO_2 flux can be attributed to live root respiration rather than biological mineralization (Pulliam, 1993). Both of these processes can be expected to be abundant in a productive and extensive swamp river system such as the AR. Soil pCO_2 has also been demonstrated to show strong seasonal and geographical variation. For example, one study described fluctuations in temperate hardwood-forested catchment soils ranging from 907 ppmv in winter to 35,313 ppmv in summer (Jones and Mullholland, 1998), while another study reported a near-constant pCO_2 of ~52,000 ppmv in undisturbed forested areas in the Amazon basin (Johnson et al., 2008). Since the Atchafalaya River basin is located in a subtropical region with seasonal variations in temperature, it likely experiences seasonal variation in rates of soil respiration and levels of soil pCO_2 similar to seasonal changes in production and respiration rates observed in its estuaries (Roberts and Doty, 2015). This would lead to high inputs of DIC from the AR basin's soils in summer and early fall, while the contribution of local soil pCO_2 to DIC loads may be expected to decrease in cooler months. The anoxic soil conditions found in wetlands provide optimal environment for the sequestration of large amounts of carbon; in fact, wetlands are estimated to store up to 30% of global soil carbon pool (Lal, 2008). Subsequently, overbank flooding of the AR may lead to further interactions with CO_2 that is sequestered in the soils of its floodplains.

2.4.2 Impacts of Floodplain Interactions

This study took place included a very wet summer, and also included unusually high winter flows. Extent of floodplain inundation during these periods almost certainly played a key role in dissolved carbon dynamics in the AR. Gauge height at Butte la Rose (BLR), is significantly related to the percentage of floodplain inundation in the 2,571 km^2 Atchafalaya Basin Floodway System (ABFS) (r^2= 0.88, p<0.01; Allen et. al, 2008) due to the gauging

station's post-channelization location. Using a prediction interval based on the findings of Allen et al. (2008), gauge height data from BLR was used to calculate the approximate percentage of the ABFS flooded at different points during this study. Approximately 61% (± 18%) of the total area of the ABFS was inundated on average during this study period, ranging from 28% in October to 89% in late January. The extent of flooding consistently exceeded the long-term mean daily statistic calculated using BLR gauge height data from 1997-2015 (Figure 2.8).

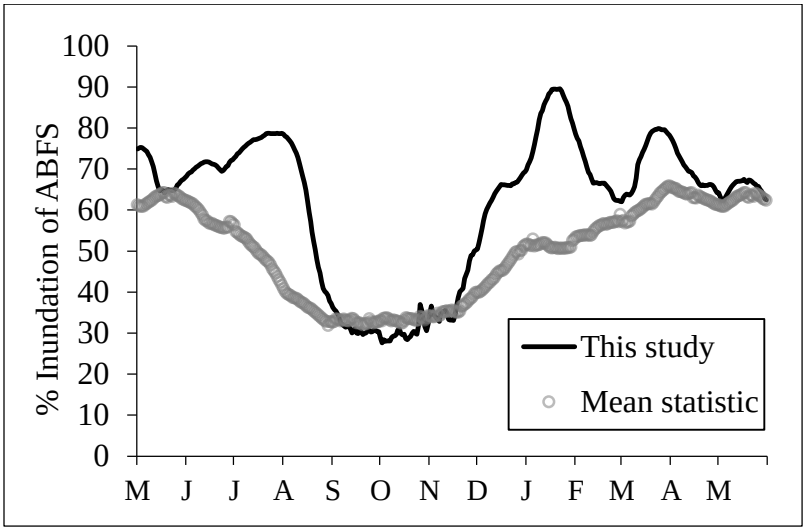

Figure 2.8. Estimated percent inundation of the ABFS for this period of study, compared to daily means calculated from data for water years 1996-2015. Data was obtained from USGS National Water Information System Web Interface (http://waterdata.usgs.gov/nwis)

During periods of greatest increase in floodplain inundation, specifically late spring and early winter, we calculated some of the greatest increases in DIC mass load from inlet to outlets (Figure 2.7, Figure 2.8), strongly suggesting that the floodplains of the AR are a major inorganic carbon source to its main channel. Wetlands are known to contribute large amounts of CO_2 to river channels (Borges et al, 2015), particularly in productive subtropical and tropical regions. In addition to interactions with soil pCO_2, other sources of DIC in the AR's floodplains should also be considered. For example, one study found that the isotopic signature of riverine CO_2 in the Amazon River was composed disproportionately of processed river-corridor and floodplain C_4

grasses, which were more bioavailable and easily degraded than other DOC sources present (Mayorga et al., 2005). Another study in the floodplains of the Amazon River demonstrated that water pCO_2 was highest when floodplains were most flooded, and attributed these heightened levels of dissolved inorganic carbon to the direct transfer of atmospheric CO_2 to the water column through wetland vascular plants, which exported half of their gross primary production to Amazonian waters (Abril et al. 2014). Increases in riverine DIC concentrations have also been reported for waters passing through rice paddies, which act as wetland systems (Wang et al., 2016). It is apparent that likewise, when the AR's floodplains are highly inundated as was seen during this study period, this extensive wetland system contributes large loads of DIC to the main channel via inputs from wetland soil and root respiration, bio-mineralization of floodplain organic material, and through washout of stored DIC in soils and backwaters. Note that greater significance of downstream change at the Wax Lake Outlet, relative to Morgan City, is likely due to greater hydraulic connectivity of the AR with floodplains in the eastern portion of the basin (Lambou and Hern, 1983).

This is especially evident in December 2015, when a winter flood-peak led to rapid inundation of the floodplain, with water reaching areas which had been severed from the main channel for several months beforehand (Figure 2.8). During December, DIC concentrations increased from Simmesport to outlet locations at Wax Lake and Morgan City by 36% and 54%, respectively, leading to the study period's largest monthly DIC mass load increase from origin to combined outlets (totaling 116.9×10^3 tonnes) (Figure 2.7). In December, pCO_2 of the river waters was relatively close to atmospheric CO_2 pressure at Simmesport (551 µatm), but increased to 2041 µatm and 905 µatm at Wax Lake and Morgan City outlets, respectively (Figure 2.4). This large increase in CO_2 pressure may be attributed to interactions with high

concentrations of soil pCO_2 stored within the typically low-flow and no-flow regions of the floodplain. Considering the tendency of wetland systems to sequester CO_2 within their anoxic soils (Bridgham et al., 2006), this is likely to be a major source of DIC during flood pulses. Tockner et al. (1999) demonstrated that different phases of river-floodplain connectivity are associated with different biological and chemical properties. Under low flow conditions (termed "phase I"), phytoplankton competed for nutrients and grazing rates were high, but during early flood stages, influx of riverine nutrients and longer water residence time favored increased biological response ("phase II"). Finally, during large overbank flood pulses ("phase III"), large washout of chemical constituents which had accumulated in floodplains was observed.

Additional evidence for the proposed "washout" of stored DIC during initial flood pulses in the AR comes from the larger downstream positive shift in $\delta^{13}C_{DIC}$ values in December than was observed during any other sampling event (from -14.78 ‰ at Simmesport, to -12.95‰ and -13.47‰ at Wax Lake and Morgan City outlets, respectively). A weak water-air pCO_2 gradient at Simmesport and a large downstream increase in pCO_2 at both outlet locations suggests relatively lower rates of atmospheric degassing. This positive shift in isotope values should then be most reflective of extensive interaction with soil-stored CO_2 and carbonate weathering, thereby describing the major source of this large change in DIC concentrations and mass loads.

Floodplain inundation was also high during annual spring flooding from May through August in 2015 (Figure 2.8), but less drastic changes in DIC concentrations, mass loads, and isotope values took place. This is probably because the ABFS had already reached a high level of inundation prior to the beginning of the sampling period. Observed changes in December were most likely a "flushing out" of soil CO_2 which had accumulated during the drier period from August through November, when the river was not extensively interacting with its floodplains

(eg.,Tockner et al., 1999). Although inundation persisted from May – August 2015, increases in DIC concentrations and mass loads were mainly seen in May and June 2015. Isotope values may have become more negative in June-July compared to May, despite relatively higher pCO_2 saturation/degassing, due to initial washout of stored soil carbonates during earlier extreme flooding events. Although sources of DIC in the AR cannot be unambiguously assigned by our data , floodplain soil interactions seem to be strongly implicated. It is clear that biogeochemical cycling of carbon is occurring in this dynamic swamp river system, and is impacting end-member dissolved inorganic carbon loads.

2.4.3 Dissolved Organic Carbon Dynamics

DOC concentrations, mass loads, and $\delta\ ^{13}C_{DOC}$, on the other hand, showed no consistent or significant trend from upstream to the downstream locations. While calculated monthly mass loads did decrease from the AR's origin to its combined outlets during 10 of the 13 sampling months (Figure 2.7), the differences in monthly mass load from inflow to outflow were not found to be statistically significant at ($p = 0.09$). With net heterotrophy indicated as one potential source of DIC increase, some loss of DOC could likewise be explained by decomposition and mineralization of organic matter, which has been found to intensify in anthropogenically altered rivers (Cai et al., 2015; Duan et al., 2007;) such as the MARS. However, since loss of DOC was far less than gain in DIC throughout the majority of this study period, it is difficult to determine how large of a role riverine DOC entering the main channel at Simmesport played. DOC in large, low-lying rivers is typically very degraded in quality (Wipfli et al., 2007), so DOC delivered to the AR via the MR may not be fresh enough to be a desirable food source, and uptake by the AR may subsequently be relatively small.

DIC production is more likely occurring largely in soils and floodplain ecosystems using fresher and more reactive sources of organic material produced within the AR Basin. A study in the MR showed dissolved organic matter in the MR to have an isotopic signature which suggests high algal association (Bianchi et al., 2003), indicating more autochthonous production than previously thought. The same may be true for the AR, since it transports much of the same water and experiences similar high nutrient fluxes in spring and summer months (Xu, 2006). Leaf litter from within the basin may also provide a further source of less degraded organic carbon for respiration, as leaf leachates as well as the breakdown of large organic materials to DOC by bacteria and fungi are major sources of DOC to waters (Cummins et al., 1972; Lush and Hynes, 1973; Otsuki and Hanya, 1972).

Organic material in the AR has been shown to be compositionally different from that of the MR, indicating significant leaf litter inputs from its landscape (Shen et al., 2012). The timing of leaf litter input within this basin corresponds with the only months where DOC mass loads increased from origin to outlet (August, September, and October; Figure 2.7). Though $\delta^{13}C_{DOC}$ did not show strong or consistent seasonal or longitudinal trends, there was a noteworthy increase in values in October and November. This supports an interpretation of a different source of DOC in fall, which may be younger based on these less negative values (ie: leaf litter). These potential in-stream and in-basin sources of fresh dissolved organic material (algal production and detrital input) may explain some portion of the disparity between calculated total mass balances, which describe significant DIC production within the basin (~0.524 Tg) and relatively lower total DOC retention (~0.243 Tg) during this study period (Table 2.4; Figure 2.7). It is important to note here that the calculated ~0.524 Tg DIC production within the basin over this study period is a conservative estimate, because it does not account for losses of CO_2 from the Atchafalaya's

waters to the atmosphere through evasion, which is very likely significant in this saturated system.

Though there were some correlations between DIC and DOC concentrations and temperature (R^2 = 0.45; R^2 = 0.34) as well as discharge (R^2 = 0.41; R^2 = 0.17) (Figure 2.9), no single parameter was clearly indicated as controlling spatial and seasonal variability in either carbon constituent. Ratios of DIC:DOC in this system were highest in summer and early fall, lowest in cooler months (Figure 2.5), and exhibited an inverse relationship to discharge trends (R^2 = 0.40, p < .0001). These ratios did not show a consistent spatial trend.

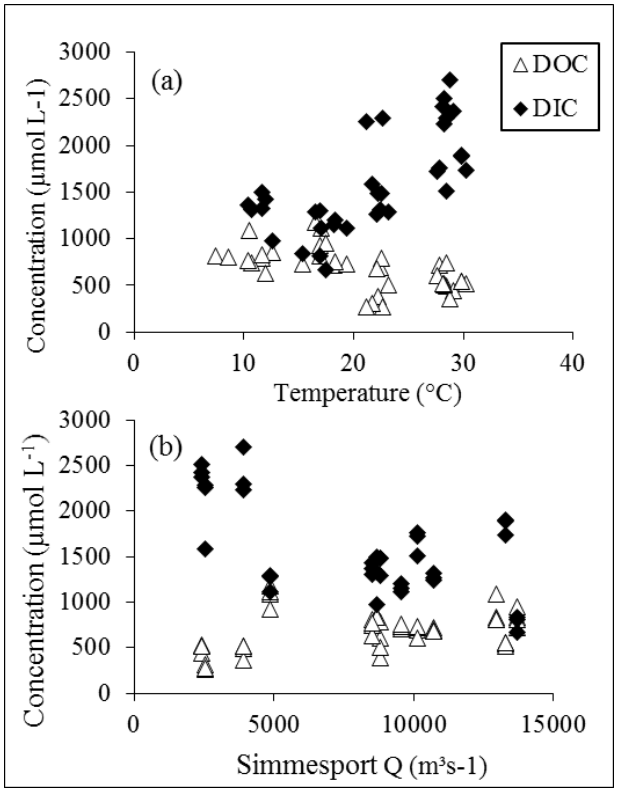

Figure 2.9 a) Relationships between DOC concentration and water temperature (y = -18.9x + 1061.9, p < .0001, R^2 = 0.34) and DIC concentration and recorded water temperature (y = 56.0x + 377.7, p < .0001, R^2 = 0.45). b) Relationships between DOC concentration and discharge at Simmesport (y = 0.02x + 478.7, p = .01, R^2 = 0.17) and DIC concentration and discharge at Simmesport (y = -0.09x + 2293.7, p < .0001, R^2 = 0.41).

The lack of downstream change in DIC:DOC ratios suggests that direct mineralization of imported riverine DOC to DIC is not the most likely path of DIC production in this system. Anticipated large increases in DIC:DOC ratios downstream in summer months, when respiration of organic matter should be highest, were not observed. This may reflect little processing of already degraded DOC, as well as rapid atmospheric degassing of CO^2.

During the period of most extensive floodplain inundation, in winter, DOC also experienced its greatest reduction in both concentration and mass load from origin to outlet. Concentrations at both outlet locations were more than 25% lower than at Simmesport. The largest loss of DOC occurred in January (~122,000 tonnes, over 45% of the DOC retention observed throughout the entire period), when inundation rose to an estimated 90% of the floodway system. This loss might be attributed to extensive interaction with typically disconnected areas of the floodplain normally containing slower-moving water, which are suspected to contain stronger microbial communities and biofilms capable of rapid biological oxidation (Battin et al., 2008; Hern and Lambou,1979) and inorganic carbon production. In addition to microbial degradation, flocculation has been described as a cause of DOC removal in low salinity waters (Benner and Opsahl, 2001). This loss of DOC during high floodplain inundation agrees with a previous study of AR total organic carbon (TOC) which showed that 83% of the variation in average monthly TOC retention in the AR was explained by average monthly inflow (Xu, 2013), where no sure mechanism for variation in retention could be constrained. A study in Australian wetlands showed that while shallow flooding led to high levels of DOC, deeper and more extensive flooding led to DOC reduction (Briggs et al., 1993); though no process is indicated, this agrees with the findings of this current study, which showed

greatest reduction in DOC mass loads during prolonged floodplain inundation. A study in the nearby forested Pearl River Basin also demonstrated that floodplain interactions can significantly alter riverine carbon fluxes by varying amounts according to season and discharge (Cai et al., 2016). The importance of floodplain interactions and associated biogeochemical processes in influencing dissolved organic carbon flux is likewise indicated in in this system.

2.4.4 Annual DOC and DIC mass load estimates

The estimated DOC mass export of 2.473 Tg from the AR into the GOM for this 13-month sampling period (Table 2.4) was higher than existing estimates would predict, but is appropriate when considering the AR's conditions throughout the study. Shen et. al (2012) compared existing estimates of annual DOC flux from the MR and AR and found that variations in estimates were largely due not to methodology, but to inter-annual variations in discharge and concentrations, with high-flow years producing nearly double the amount of DOC observed in low-flow years. Discharge at Simmesport during this sampling period was 37% higher than the long term annual average (6,547 $m^3 s^{-1}$) reported by Xu (2006). The reported average concentration of 673 ± 218 μmol DOC L^{-1} at the AR's outlets was 74% higher than the long-term (1996-2010) annual average, and the calculated mass flux of DOC reported during this 13-month study is more than double the long-term estimate for the AR (386 ± 111 μmol L^{-1}; 0.95 Tg yr^{-1}) found by Shen et al. (2012). Though this difference is large, it is not unjustified. Organic matter has been shown to be transported disproportionately during high flows and storm events (Kiffney et al., 2000; Tian et al., 2015; Wallace et al., 1995).

The effects of high precipitation and discharge on dissolved carbon fluxes is evident in this study due to an unusually warm and wet winter across the MR watershed associated with a

strong El Niño year and a series of winter storms. In the AR, seasonal peak discharge normally occurs in the spring as a result of snowmelt in northern tributaries (Lambou and Hern, 1983). Similarly, according to long-term averages, DOC export from the MR and AR, which generally follows the hydrograph, should increase in December and crest between April and June (Shen et al., 2012; Xu, 2013). During our study, however, both discharge and DOC flux peaked in winter. Mean discharge reported for this study is higher than annual averages not only due to high flow, but also partially because of the timing of our sampling events, which did not begin and end according to a normal water year (October-October) or a normal calendar year. Sampling began during cresting spring discharge in 2015, extended through a second larger peak in winter, and continued through cresting spring discharge in 2016 (Figure 2.2), thereby encompassing more high-flow periods than typical annual averages and estimates. All of these peaks also exceeded USGS reported median daily statistics. Our dissolved organic carbon mass load estimates are proportionally affected.

Table 2.4. Summary of DIC and DOC mass flux and balance for the entire sampling period from May 1, 2015 to May 31, 2016. Negative values indicate loss from origin to outlet. Different letters within a column indicate significant difference (α=0.05).

Location		Q (km^3)	DIC mass load (Tg)	DOC mass load (Tg)
Input	Simmesport	305.342[a]	4.822[a]	2.717[a]
Output	Wax Lake	136.619	2.440	1.167
	Morgan City	163.694	2.905	1.307
	Combined	300.313[a]	5.346[b]	2.473[a]
Balance	(Output-Input)	-5.030	0.524	-0.243

Total estimated DIC loading into the NGOM calculated for this 13-month sampling period was 5.346 Tg DIC. This represents the first estimate of DIC flux from the AR. This new

estimate agrees proportionally with existing literature describing MR DIC flux; it is an approximate one-third of a 2008 estimate of the MR's average annual DIC load, ~15 Tg DIC yr^{-1}, made using daily alkalinity measurements recorded in New Orleans, LA (Raymond et al., 2008). There are currently no other available estimates of AR DIC flux with which to compare magnitude. The year of 2008 and our study year were both high flow years of the Mississippi-Atchafalaya Rivers. Future studies are needed to determine mass proportion of DIC and DOC between the two rivers under low flow conditions.

Due to the higher-than-average discharge and floodplain inundation seen during this 13-month study period, these estimates should serve to illustrate the potential effects of climate extremes on riverine dissolved carbon dynamics. Other studies have previously demonstrated that climate extremes result in increased loads of organic carbon (Tian et al., 2015; Yoon and Raymond, 2012), similar to the high estimate of DOC export calculated during this high-flow study period. Temperature and precipitation have been demonstrated to account for the greatest portion of seasonal and annual variability in estimates of organic and inorganic carbon export (Tian et al., 2015), making DIC and DOC estimates during unusually warm and wet years, such as the year spanned by this study, of high interest in light of increases in both river discharge and temperatures projected by climate change models (Kundzewicz et al., 2008; Ren et al., 2015). The results of this study provide evidence that during high discharge events, the extensive floodway system in the Atchafalaya River Basin may provide a suitable environment for the removal of excess dissolved organic carbon within its floodplains, with corresponding increases in DIC export and atmospheric degassing. Such information can be useful for future management of nutrient and carbon fluxes into the NGOM, as the discharge of the Mississippi is projected to increase largely by the end of this century (i.e. ~11-60%, Tao et al., 2014).

2.5 Conclusions

This study demonstrates that a large river with extensive floodplains in its coastal margin can act as a significant source of dissolved inorganic carbon both to coastal systems and to the atmosphere, and may also be important sinks for dissolved organic carbon. This effect is particularly pronounced during higher-than-average flow periods where extensive interactions between river and floodplain soils and backwaters are able to take place, especially during initial flood stages. The influence of floodplain interactions on biogeochemical cycling of carbon in this system may be due to a net heterotrophic response to high productivity within this large subtropical river swamp system, with high CO_2 production occurring in floodplain soils, vascular plant root zones, and in the water column. This is indicated by trends in dissolved carbon concentrations, mass loads, and isotopic composition from inlet to outlet locations, as well as seasonal trends in pCO_2 and DIC:DOC throughout the study period. This study was conducted during an abnormally wet summer and winter, which resulted in very high flow and high mass exports of dissolved organic and inorganic carbon into the Northern Gulf of Mexico. These results are of particular interest as we continue to evaluate changes in riverine carbon transport and processing in light of our rapidly changing climate. As discharge of many of the world's rivers are projected to increase in coming years due to global warming and intensified hydrological cycling, increased carbon fluxes to coastal zones should be anticipated. Low-lying floodplain systems such as the studied Atchafalaya River must be taken into account when examining modern carbon budgets, and may need to be looked to in future years for the filtration and removal of organic materials, which impact coastal margins and ocean ecosystems as a whole.

CHAPTER 3: CONTRIBUTION OF THE RED RIVER TO DISSOLVED CARBON COMPOSITION IN THE ATCHAFALAYA RIVER

3.1 Introduction

The quantity and quality of carbon exported by rivers to coastal margins has important impacts on marine ecosystem health and functioning, and is important to the development of global carbon budgets (Chavez and Takahashi, 2007; Tank et al., 2013). Studies have shown substantial increases in the global riverine export of terrestrial carbon to oceans over the past several decades, and have linked these increases to human activity such as changes in land use, urbanization, and intensive agriculture (Butman et al., 2015; Evans et al., 2005; Ren et al., 2015). The Mississippi River (MR) is the largest river in North America, and is among the largest in the world, making its carbon export globally significant (Bianchi et al., 2004, 2007; Raymond and Cole, 2003; Cai et al., 2008). This massive river system drains approximately 41% of the contiguous United States and covers large areas of intensively farmed land, heavily urbanized areas, and population hubs (Goolsby and Battaglin, 2001). Extensive human alteration of this 3,230,000 km² basin has resulted in recent large increases in anthropogenic carbon and nutrient export (Raymond et. al 2008; Turner and Rabalais, 1991). In south-central Louisiana, ~25% of the flow of this immense river is diverted from its highly engineered channel into the Atchafalaya River (AR), a large (~275 km long) braided river-floodplain system. The AR and the MR both discharge high volumes of water and dissolved and particulate matter into the Northern Gulf of Mexico (NGOM), where the inputs of these major rivers heavily impact estuarine and coastal processes (Meiggs and Taillefert, 2011).

Regions of the NGOM dominated by the Mississippi-Atchafalaya River System (MARS) plume have demonstrated greatly enhanced productivity as well disruption of natural

biogeochemical cycling (Donner et al., 2004; Lohrenz et al., 1997). Inputs of anthropogenic riverine carbon play a role in this ecosystem disruption; for example, organic matter exported by the MARS may contribute up to 23% of the O_2 demand necessary for the perpetuation of seasonal severe hypoxic conditions in the Gulf of Mexico (Green et al., 2006; Justic et al., 1997). Though coastal systems have gained increasing recognition as influential components of global carbon budgets (IPCC 2013; Aufdenkampe et al, 2011), carbon dynamics in coastal regions such as the NGOM remain complicated and poorly characterized due to lack of geographically specific estimates of carbon export (Chavez and Takahashi, 2007), preventing integration into global carbon assessments. Though the MR has been well studied, carbon constituents in the large and influential AR swamp-river basin remain poorly characterized.

After passing through the Old River Control Structure (ORCS) in southern Louisiana, the diverted portion (~25%) of the MR is joined by the entire flow of the Red River (RR) from Texas, together forming the Atchafalaya River. The less anthropogenically altered RR may have a large influence on both the quantity and quality of riverine dissolved inorganic carbon (DIC) and dissolved inorganic carbon (DOC) passing through the MR's largest distributary into the Northern Gulf of Mexico (NGOM). The fraction of the Atchafalaya River's flow contributed by the RR can vary anywhere from 7% to 70% throughout a given year (Xu and BryantMason, 2011). The waters of the AR therefore display large temporal variations in chemical composition according to the relative contributions of its tributaries. For example, a study on nitrate in this system concluded that although approximately one-third of the Atchafalaya River's average flow came from the RR, a nearly negligible 3% of the AR's total mass load of nitrate was delivered by the RR (Xu and BryantMason, 2011). This means that the RR has the capacity to play an important role in diluting the large loads of nutrients entering the NGOM from the agriculturally

dominated and Mississippi River watershed. The RR may then also differ greatly from the diverted portion of the MR in terms of dissolved carbon mass constituents delivered to the AR. The potential dilution effect of the RR on the MR's anthropogenically enhanced DIC and DOC loads is therefore critically important to consider when evaluating the export of dissolved carbon from the MARS into coastal systems.

In addition to potential differences in total mass contributions of dissolved carbon from these two large tributaries to the Atchafalaya River, the RR and MR may also exhibit important differences in the source and quality of the dissolved carbon they deliver. DOC in the MR has been demonstrated to be largely refractory, with only about 3% of DOC contributing to the labile carbon pool (Benner and Opsahl, 2001). Based on analysis of DOC, lignin-phenols, amino acids, and neutral sugars, DOC in the AR has already been demonstrated to be more bioavailable and of higher quality than DOC in the MR (Shen et. al, 2012). However, the RR's potential importance as a source for this more labile organic material remains poorly investigated. More bioavailable DOC can be quickly processed in large floodplains such as the AR (Xu, 2013; Battin et al., 2008) and mineralized to DIC, which can in turn lead to increased outgassing of riverine DIC to the atmosphere in the form of CO_2 (Mayorga et al., 2005), as well as increased chemical weathering (Iwara et al., 2013). Dissolved carbon inputs into the AR from the RR, however, have not yet been well characterized; information on differences in composition and quality of carbon inputs from these tributaries are sorely lacking.

Riverine stable carbon isotope analysis describes the ratio of $^{13}C/^{12}C$ in a sample of water, which can be used to identify major sources of dissolved carbon as it interacts with the atmosphere, sediment, and biosphere; isotopic constraining of carbon sources and in-stream processing provides useful information regarding the quality of carbon constituents. The $\delta^{13}C$

signature of the atmosphere, for example, is ~ -7.5‰ (Mook et al., 1983). When this atmospheric carbon is taken up by plants during photosynthesis, the lighter isotope is preferentially used, producing a much lower $\delta^{13}C$ signature in plants. Plants using the C3 pathway, which represents the majority of terrestrial vegetation, generally have $\delta^{13}C$ values between -24 to -34‰, while C4 plants have less negative values ranging from -6 to -19 ‰ (Deines, 1980). Carbon stored in soils by the biological oxidation of organic matter exhibit average $\delta^{\mathbf{13}}C$ values of -27‰ in soils dominated by C3 plants, and around -14% in soils dominated by C4 plants (Ehleringer and Cerling, 2002; Salomons and Mook, 1986; O'Leary, 1988; Vogel, 1993), both of which may become enriched by diffusion processes (Cerling et al., 1991). Within aquatic systems, the $\delta^{13}C$ values of these terrestrially-derived carbon sources are further impacted by riverine biogeochemical processes; photosynthesis and atmospheric degassing preferentially remove ^{12}C (Baird et al., 2001) which leaves the remaining aquatic carbon pool enriched in $^{\mathbf{13}}C$, resulting in a positive shift in $\delta^{\mathbf{13}}C$ values; meanwhile respiration processes contribute to $^{\mathbf{13}}C$ uptake, and subsequently more negative isotope values (Dubois et al., 2010). Studying isotopic composition of dissolved carbon in the RR and MR outflows into the AR may provide useful insight into potential sources and processes responsible for dissolved carbon constituents entering the Atchafalaya River Basin, reflecting water quality and ecological functioning.

This study aimed to investigate the impact of the Red River on carbon dynamics in a major distributary of the Mississippi River, the Atchafalaya River. Specifically, the study set out to 1) collect water samples and conduct in-situ water quality measurements at locations near the confluence of the MR and RR over a 1-year period; 2) analyze riverine dissolved organic and inorganic carbon concentrations in these major tributaries; and 3) determine isotopic signature of $\delta^{\mathbf{13}}C$ to identify composition and source of dissolved organic and inorganic carbon at a wide

range of flow conditions and relative discharge contributions by the Red River. The data collected in this study describes how the waters of the Atchafalaya River are compositionally affected, in terms of both quantity and quality of dissolved carbon constituents, by the relative chemical contributions of the Red River.

3.2 Methods

3.2.1 Study Area

This study was conducted at the confluence of the Red River and the Mississippi River diversion at the ORCS in central Louisiana, USA (Figure 3.1). The 2,189 km long Red River originates from northwestern Texas and flows eastward to Oklahoma and Arkansas and north Louisiana before joining the diverted water from the Mississippi to form the Atchafalaya River (Fig. 1). The Red River basin drains 169,890 km^2 of land, passing through a wide variety of ecosystems and environmental conditions. The RR's headwaters originate in a semiarid climate, with an upper main stem which occasionally lacks flow altogether (Matthews et al., 2005); however, as it flows east it encounters a subtropical humid environment, with annual precipitation reaching ~1500 mm at its confluence in central Louisiana. The western portion of the river flows through areas composed of 40 – 60% rangeland and 30% cropland, while the eastern portion is 50% forested, 20% cropland, and only 10% pasture. The RR's watershed is thus very different than that of the Mississippi River, which is predominately cropland (58%) and drains a land area of over 3 million km^2.

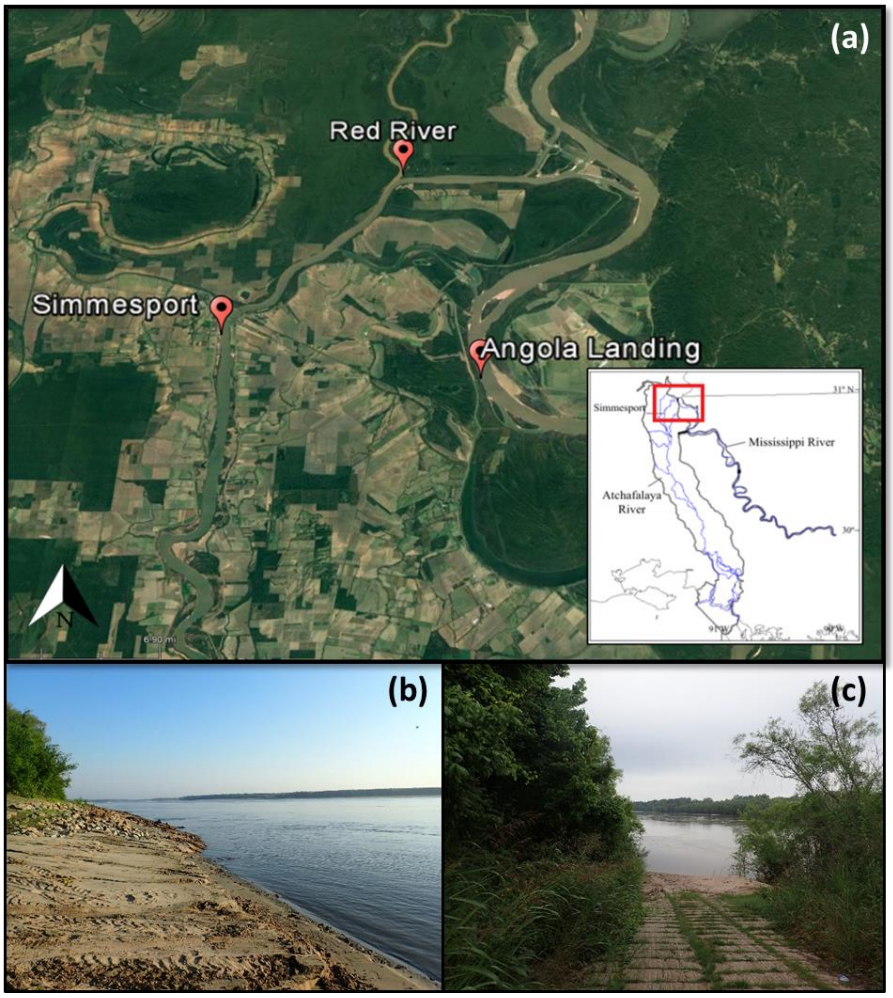

Figure 3.1 Geographical location of the Old River Control Structure, where ~25% of the Mississippi River's water is diverted to join the entire flow of the Red River, forming North America largest swamp river (the AR). In this study, water quality samples were collected at a sampling location on the Red River and on the Mississippi River at Angola Landing (marked).

3.2.2 Water Sampling and Field Measurements

From May 13, 2015 to May 19, 2016, monthly field trips were made to collect water samples and perform in-stream measurements at the Mississippi River (Angola Landing, LA, Fig. 3.1), Red River (about 400 m above the conference of the Red River and Old River Outflow Channel) and Atchafalaya (Simmesport, LA). Sampling trips were conducted over a wide range of flow conditions (Fig. 3.2), with 4 sampling trips taking place during low flow conditions and 8 trips

taking place during high flow conditions based on the long term average reported by Xu (2006). Additionally, several trips took place during periods where the Red River contributed a higher percentage of flow to the Atchafalaya River than did the Mississippi River, offering greater sample diversity.

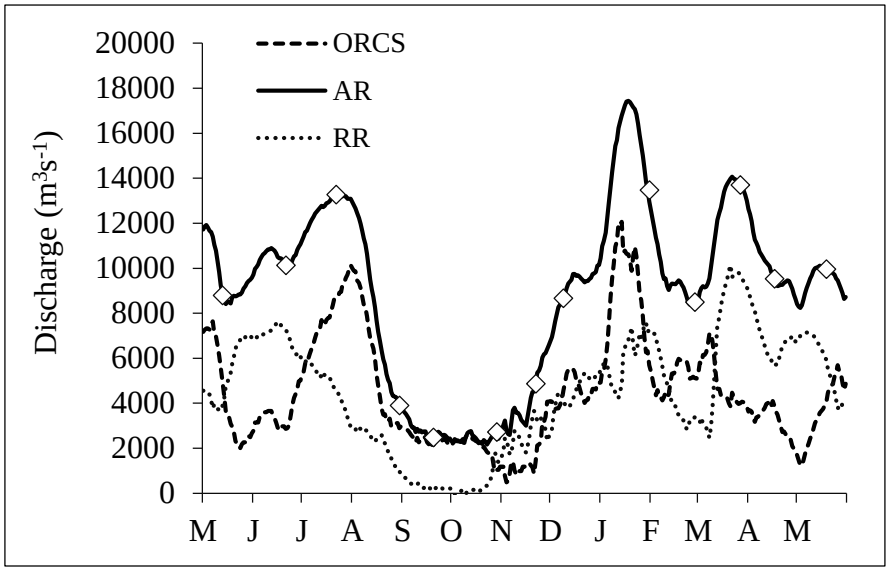

Figure 3.2. Inflows from the Mississippi River's ORCS and the Red River into the AR at Simmesport from May 2015 – May 31, 2016. Diamonds depict water quality sampling/field measurement dates.

During each monthly sampling event, ambient parameters including dissolved oxygen (DO), pH, temperature, and specific conductance were recorded using a YSI 556 multi-probe meter (YSI Inc., Yellow Springs, OH, USA) at each location. Phycocyanin Fluorescence was recorded using an Aquafluor 8000-010 handheld fluorometer (Turner Designs, San Jose, CA, USA). At each site, composite surface water samples were collected approximately 50 cm below the river surface. Samples for DOC analysis were stored in 250-ml High Density Polyethylene (HDPE) bottles. Samples for DIC analysis were septum-capped in 20 mL glass vials and immediately placed on ice, along with DOC samples. All bottles for DIC stable isotope analyses

were filled without headspace, closed with butyl rubber/PTFE septa. All bottles were thoroughly acid-cleaned and rinsed using river water before use. Duplicate samples were collected at one site per trip for quality control purposes. All water samples were stored in a cooler with wet ice during transportation. DIC samples were refrigerated until chemical analysis, while DOC samples were filtered and frozen immediately upon return from sampling.

3.2.3 Sample Analysis

Upon returning to the lab, samples to be analyzed for DOC and DIC are shipped frozen on ice to University of California Davis Stable Isotope Facility, which provides δ ^{13}C isotope analysis of DIC by trace gas using a GasBench II system interfaced to a Delta V Plus IRMS (Thermo Scientific, Bremen, Germany.) Precision of measurements was better than 0.1%.

DOC is analyzed for ^{13}C using an O.I. Analytical Model 1030 TOC Analyzer (OI Analytical, College Station, TX) interfaced to an isotope ratio mass spectrometer (Sercon Ltd., Cheshire, UK) utilizing a gas-trap interface. Samples are acidified and purged with helium off-line to remove all dissolved inorganic carbon (DIC). The remaining sample is reacted with sodium persulfate to convert DOC into a pulse of CO_2, which is carried in a helium flow to the isotope ratio mass spectrometer where the $^{13}C/^{12}C$ ratios are measured. Samples are corrected based on included laboratory standards calibrated against NIST Standard Reference Materials with a precision of measurements better than 0.4%. These methods also provide values for DIC and DOC concentrations using concentration calibration curves developed using known references. Error for DOC and DIC concentration calculations was better than 5%.

Stable isotope values are expressed as deviations per mil (‰) from Vienna Pee Dee Belemnite (VPDB), a standard reference material based on the ratio of $^{13}C/^{12}C$ found in a highly ^{13}C-rich belemnite fossil according to the formula

$$\partial\ 13C\ ‰ = \left(\frac{R_{sample}}{R_{standard}} - 1\right) * 1000$$

where R is the ratio of the numbers (n) of the heavy and light isotope of an carbon ($^{13}C/^{12}C$) in the sample and the reference (Coplen, 2011).

3.2.4 Carbon Mass Transport Calculation

To best estimate dissolved carbon loading with monthly sampling data, rating curves were modelled to determine relationships between discharge and DIC and DOC for the Red River and the Mississippi River's ORCS. The basic power law model:

$$L = aQ^b \qquad (1)$$

which can be log-transformed to:

$$\ln L\ =\ \ln a\ +\ b\ln Q\ +\ \varepsilon \qquad (2)$$

where L is daily mass load of dissolved carbon constituents (in tonnes), Q is daily discharge, and ε is an error term assumed to be normally distributed.

The model parameters were determined using the SAS 9.4 software package (SAS Institute) the following equations were produced for the estimation of DIC and DOC daily mass loads:

$$\ln LorcsDIC\ =\ -8.79947\ +\ 0.90289\ln Qorcs \quad (3)$$

$$\ln LredDIC\ =\ -4.95663\ +\ 0.66734\ln Qred \quad (4)$$

$$\ln LorcsDOC\ =\ -17.41285\ +\ 1.27491\ln Qorcs \quad (5)$$

$$\ln LredDOC\ =\ -15.45946\ +\ 1.20420\ln Qred \quad (6)$$

where *Lorcs* and *Lred* are daily dissolved carbon loads (in tonnes) flowing from the Mississippi River's ORCS and from the Red River, respectively, *Qorcs* is daily discharge in cubic metres diverted from the MR through the ORCS, and *QRed* is the daily discharge of the Red River calculated by:

$$Qred = Qatch - Qorcs \quad (7)$$

where *Qatch* is the daily discharge of the Atchafalaya River at Simmesport.

Equations (3) ,(4), (5), and (6) have regression coefficients (R^2) of 0.85 , 0.92, 0.90, and 0.96, respectively.

3.2.5 Estimation of riverine pCO_2

The partial pressure of carbon dioxide in water was calculated according to the method shown by Cai and Wang (1998), which uses DIC concentration and measured pH data in the equation:

$$pCO_2 = \frac{[CO_2]}{K_H} = \frac{C_T \{H\}^2}{(\{H\}^2 + \{H\}K_1 + K_1K_2)K_H}$$

where C_T is the measured DIC value in ?, $\{H\} = 10^{-pH}$, K_H is the solubility constant (Weiss, 1974), and K_1 and K_2 are the dissociation constants of carbonic acid. Since sampled waters possessed salinity measurements of less than 0.2, the K_1 and K_2 of Harned and Davis (1943) and Harned and Scholes (1941) were used, respectively, for salinities near 0. K_H, K_1 and K_2 are all adjusted for absolute temperature.

3.3 Results

3.3.1 River Flow and Ambient Conditions

During the study period from May 2015 through May 2016, the flow of the Red River entering the Atchafalaya River, computed as the difference between the discharge at Simmesport and the diverted flow from the Mississippi River at the Old River Control Structure, averaged 4,429 ± 2,550 (standard deviation) $m^3 s^{-1}$, ranging from negligible flow in the fall to 10,137 $m^3 s^{-1}$ in March. Mean daily discharge from the Old River outflow channel into the Atchafalaya was 4,473 ± 2,477 $m^3 s^{-1}$, with a minimum flow rate of 481 $m^3 s^{-1}$ in November and a maximum discharge of 12,063 $m^3 s^{-1}$ in January. The combined flow from the two rivers averaged 8,901 ± 3,885 $m^3 s^{-1}$ at Simmesport, falling as low as 2,166 $m^3 s^{-1}$ in late October and reaching a maximum rate of 17,443 $m^3 s^{-1}$ in mid-January. On average, the Red River contributed ~46.5% (± 21%) of the Atchafalaya River's flow, with a maximum contribution of ~85% in April 2016. The waters of the Red River made up a greater portion of the AR's flow at Simmesport than did the MR during this sampling period 47.6% of the time (n = 397). Mean daily discharge rates varied somewhat dramatically by season. Lowest average daily flows at Simmesport occurred throughout fall (3,126 $m^3 s^{-1}$), followed by summer (10,401 $m^3 s^{-1}$) and spring (10,619 $m^3 s^{-1}$), with highest average daily flow occurring in winter (11,234 $m^3 s^{-1}$).

It is important to note that discharge at Simmesport during this 13-month period (8,901 $m^3 s^{-1}$) was much higher than the long-term (1978-2004) annual average (6,547 $m^3 s^{-1}$) reported by Xu (2006), and also exceeded values reported by USGS from WY 2010-2015, which averaged 6,187 $m^3 s^{-1}$ (with yearly averages ranging from 4,967 to 7,229 $m^3 s^{-1}$). Hence, the wet year may have discharged higher quantities of carbon and other elements.

Waters of the Red River showed significantly higher temperature ($p<.0001$) and phycocyanin fluorescence ($p = 0.046$), but no significant differences in dissolved oxygen saturation, turbidity, or pH (Table 1). Fluorescence ranged from 26.23 AFU (Sept 2015) to 109.90 AFU (Feb 2016) in the Mississippi River and from 27.02 AFU (Sept 2015) to 223.40 AFU (Dec 2015) in the Red River.

Table 3.1. Average ambient conditions of waters of the Mississippi River at Angola and the Red River at the confluence with the Mississippi River. The different letters within a column indicate significant difference ($\alpha=0.05$).

Site	Temperature (°C)	DO (%)	pH	Fluorescence (AFU)	Turbidity
MR	18.0 ± 8.0^a	84.6 ± 24.1^a	7.3 ± 0.9^a	61.9 ± 26.5^a	80.2 ± 45.9^a
RR	21.4 ± 7.1^b	75.4 ± 24.6^a	7.6 ± 0.6^a	86.1 ± 47.9^b	113.7 ± 75.6^a

3.3.2 DOC and DIC Concentrations and Ratios

Dissolved organic carbon and dissolved inorganic carbon concentrations showed clear distinction between the waters of the RR and MR. DOC concentrations in the Red River were significantly higher than in samples collected from the MR,typically nearly twice as high (177% ± 39% higher on average), while the RR's DIC concentrations were typically half of those found in the MR at Angola (49.2% ± 11% lower) (Table 2.2). The variable mixing of the waters of these two rivers to form the Atchafalaya therefore results in complex trends in dissolved carbon at Simmesport, depending on the relative contribution of each river at any given point on the hydrograph.

The mean concentrations of DOC measured in the RR and in the MR at Angola, respectively, were 871 ± 249 µmol C L^{-1} and 509 ± 133 µmol C L^{-1}. The mean concentrations of

DIC measured in the RR and the MR at Angola, respectively, were 1034 ± 407 µmol C L^{-1} and 1795 ± 510 µmol C L^{-1} . Reported values for each sampling trip can be seen in Table 2.2.

Table 3.2. DOC and DIC concentrations (µmol L^{-1}) in the RR and MR during each sampling event. Different letters in averages indicate a statistically significant difference (α= 0.05).

	DOC		DIC	
	RR	MR	RR	MR
5/13/2015	1225	454	718	1993
6/21/2015	692		1343	
7/22/2015	749	451	1148	2052
8/30/2015	533	465	1582	2345
9/20/2015	678	336	1927	2667
10/29/2015	433	229	1051	2027
11/22/2015	1169	640	750	1908
12/9/2015	914	552	895	1766
1/31/2016	1139	711		
2/28/2016	1034	583	804	1586
3/27/2016	1044	502	511	1048
4/17/2016	917	567	759	2019
5/19/2016	801	610	928	1921
Average	871[a]	509[b]	1035[c]	1939[d]
Std dev	±249	±133	±407	±409

During the period of low flow from August through November, DOC fell to somewhat lower concentrations relative to the rest of the sampling period, while DIC concentrations were relatively heightened. DIC was highest in the RR in August and September and lowest in March, and DIC in the MR showed the same trend. The RR's DOC concentration was measured at its lowest in October and highest in May 2015, and the MR's DOC concentration was also lowest in October, but highest in January.

The ratios of DIC:DOC in these two rivers also differed greatly (Figure 3.3). The MR's mean DIC:DOC was 4.4, and never fell below 2. The ratio of DIC to DOC in the MR was especially high (nearing 9) during September and October, when DOC in the MR dropped to lowest observed concentrations (Table 3.2). The RR's DIC:DOC , however, was generally below 1, and never exceeded 3. Seasonal variations in DIC:DOC in the RR were less extreme than those in the MR, but showed similar increase in fall months.

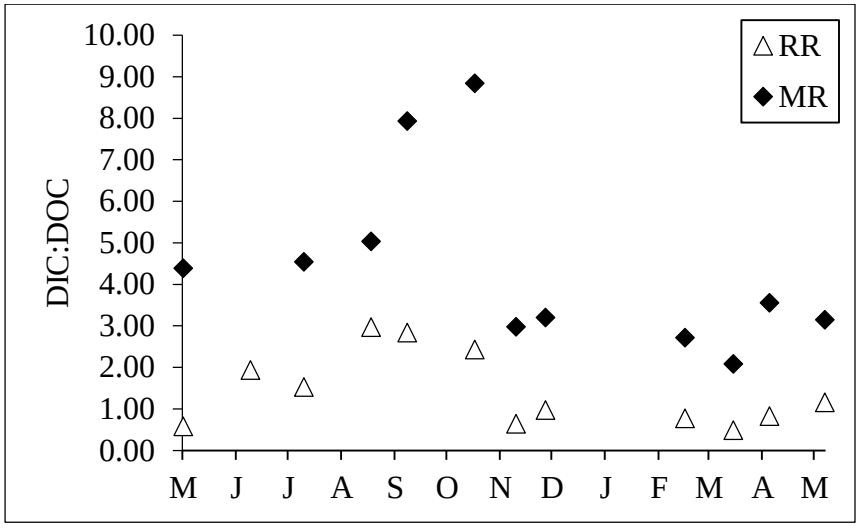

Figure 3.3. Ratio of DIC to DOC in the Atchafalaya River's two tributaries before their confluence on monthly sampling dates from May 2015 to May 2016.

3.3.3 pCO_2 fluctuations

Based on calculated pCO_2, waters from both rivers were found to be consistently saturated with CO_2 relative to atmospheric pressure (Figure 3.4). The MR was significantly more saturated than the RR in terms of pCO_2 ($p = 0.012$). Carbon dioxide pressure in the MR ranged from 730 µatm (Mar 2016) to 3595 µatm (May 2015), and from 227 µatm (Dec 2015) to 3328 µatm (May 2015) in the RR, and both rivers showed lower pCO_2 in the winter and higher pCO_2 in the

summer. pCO_2 could not be calculated for either site in Jan 2016 due to lack of DIC measurements, or in Mar 2016 due to pH probe malfunction.

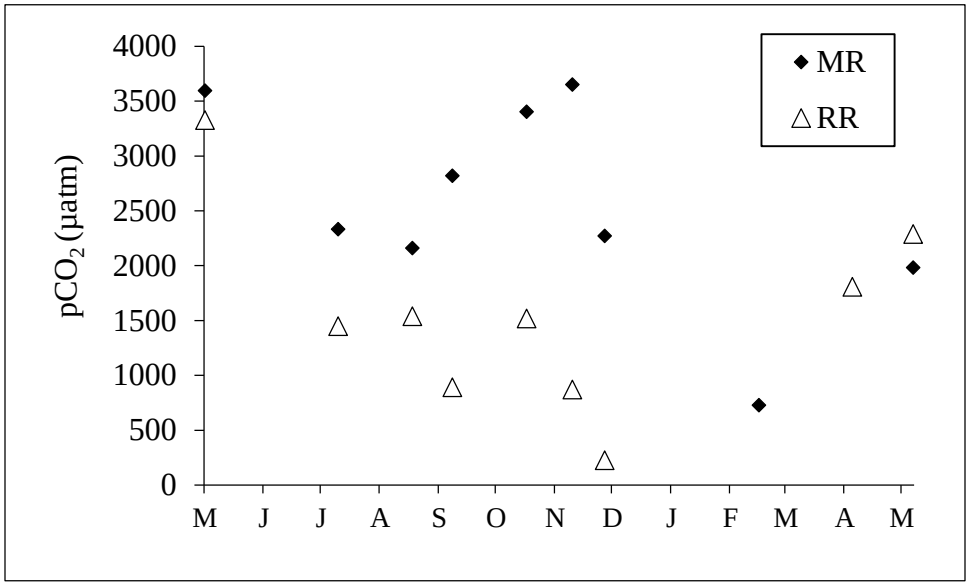

Figure 3.4. Calculated pCO_2 in the Atchafalaya River's two tributaries before their confluence from sampling dates from May 2015 to May 2016 (no calculation is available for sampling events on 1/31/2016 or 3/27/2016).

3.3.4 DOC and DIC Mass Transport

For the sampling period, the discharge rating curve model estimated that the Red River contributed 1.41 teragrams (Tg) of the 4.76 Tg DIC calculated mass load passing through the Atchafalaya River at Simmesport (or, 29.7% of total DIC) and 1.74 Tg of the 2.75 Tg DOC calculated mass load passing through Simmesport (or, 63.2 % of total DOC). The relative contributions of the Red River and the Mississippi River to the AR's dissolved carbon budget varied seasonally according largely to discharge. On average, the Red River contributed 30.8% (± 13.9%) of the daily total DIC mass load to the Atchafalaya River, ranging from negligible contributions when discharge was minimal, to a maximum of upwards of 65% in November 2015 and May 2016 when RR's waters made up more than 80% of the AR's flow (Figure 3.5).

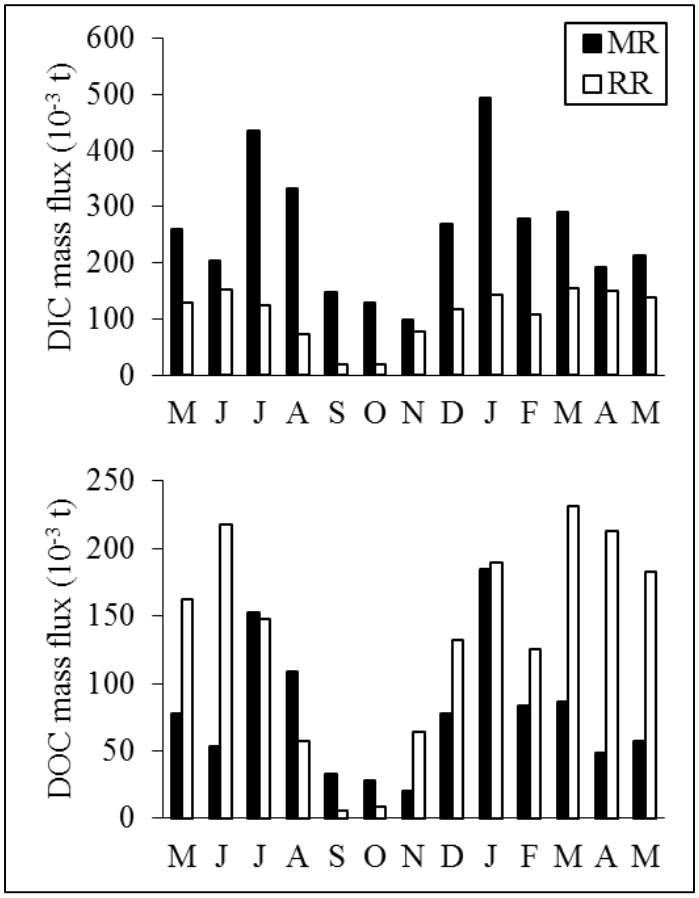

Figure 3.5. Monthly mass fluxes of DIC and DOC of the Misssippi River at the ORCS and Red River before the confluence with the Old River.

The Red River's total contribution to DOC mass loading in the AR was disproportionately high, especially in comparison to its contribution to DIC flux (Figure 3.5). On average, the Red River contributed 57.5% (± 24.4%) of the daily total DOC mass load to the AR, ranging from negligible contributions when discharge was minimal, to maximums of greater than 90% in November 2015 and May 2016. The RR frequently contributed a greater percentage of the AR's DOC mass load than did the MR (observed on 62% of n = 397 days). However, it rarely contributed a greater portion of the Atchafalaya's total DIC (observed on 8% of n = 397 days).

3.3.5 Isotopic signature of dissolved carbon

$\delta^{13}C_{DIC}$ values varied significantly between the RR and MR ($p < .0001$), which had average values of -15.3 ± 1.9 and -12.0 ± 0.9 (‰ vpbd), respectively (Figure 3.6). Both tributaries showed enrichment in $^{13}C_{DIC}$ throughout summer before becoming more depleted throughout late fall and winter. $\delta^{13}C_{DIC}$ values in the RR showed a strong relationship with DIC concentrations ($R^2 = 0.71$, $p = .006$), but $\delta^{13}C_{DIC}$ values in the MR showed no significant relationship with DIC concentrations ($R^2 = 0.21$, $p = 0.15$).

$\delta^{13}C_{DOC}$ values were also found to differ significantly between the AR's two tributaries ($p = 0.03$). Average values in the RR and MR were -28.3 ± 0.6 and -27.8 ± 0.5 (‰ vpbd), respectively (Fig. 3.5). DOC in the RR was generally slightly more depleted in ^{13}C than the MR. There was no clear seasonality of $\delta^{13}C_{DOC}$ values; depletion and enrichment was somewhat chaotic throughout the study, but both rivers showed a similar overall trend.The majority of values remained well within the range of -27 to -29 (‰ vpbd) for all sampling locations. Isotopic composition of DOC did not exhibit significant correlation with DOC concentration values at either site (RR: $R^2 = 0.28$, $p = 0.06$; MR: $R^2 = 0.01$, $p = 0.75$) and was not clearly related to any seasonal trends in DOC concentrations.

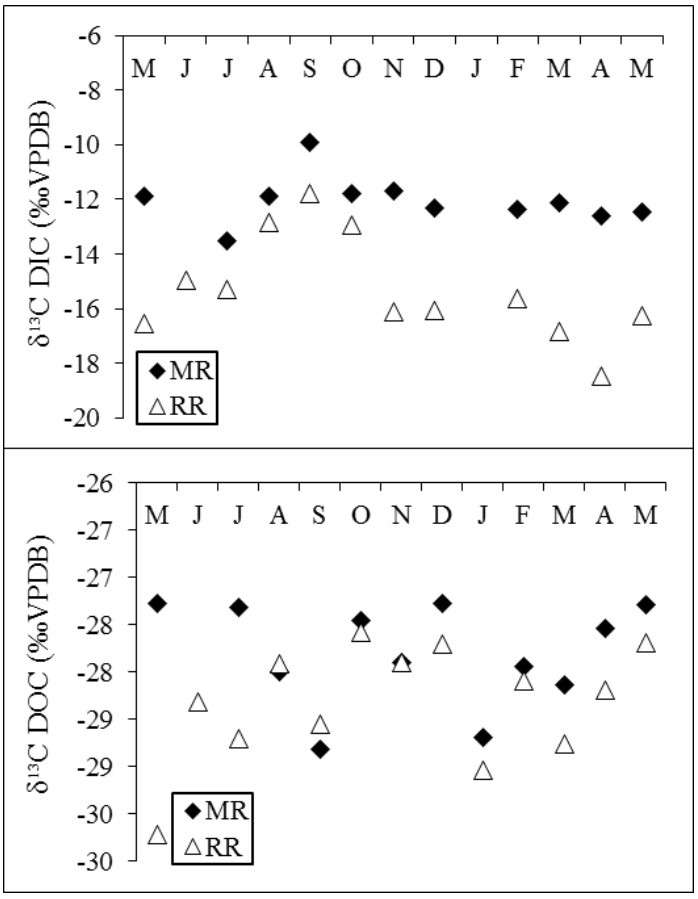

Figure 3.6. δ $^{13}C_{DIC}$ (‰ VPDB) and δ $^{13}C_{DOC}$ (‰ VPDB) signatures in the AR's two major tributaries, the RR and MR, before their confluence.

3.4 Discussion

3.4.1 Red River Influence on AR Carbon Concentrations and Mass Loads

The Red River significantly impacted dissolved carbon loading in the Atchafalaya River. The Red River's average contribution to DOC mass loading in the Atchafalaya River was much greater than its contribution to DIC mass loading. The RR more often than not contributed greater amounts of DOC than did the MR, but its estimated contribution to DIC mass loading was lesser than that of the MR during 92% of the study period. Overall, the Red River contributed 1.41 teragrams (Tg) of the 4.76 Tg DIC calculated mass load passing through the

Atchafalaya River at Simmesport (or, 29.7% of total DIC) and 1.74 Tg of the 2.75 Tg DOC calculated mass load passing through Simmesport (or, 63.2 % of total DOC).

A 2012 study attempted to characterize AR and MR DOC using chromophoric dissolved organic matter, total dissolved lignin phenols, amino acids, and neutral sugars during five cruises in the NGOM (Shen et al., 2012). The study suggested that the RR may account for ~13% of the elevated DOC concentrations in the AR compared to the MR, attributing the remainder to inputs from the AR's floodplains. This present study suggests, however, that the RR may have a much greater contribution to DOC mass loading in the AR than has been previously indicated. If the majority of elevated DOC concentrations in the AR's discharge plume originate from within the AR's basin (Shen et al., 2012), it is possible that the increased loads of DOC contributed by the RR (this study) are rapidly mineralized within the floodplains of the AR and subsequently replaced by organic inputs from the swamp-river basin. If true, the RR may contributing young and highly reactive organic material to the AR, which would likely be consumed rapidly when mixed with the nutrient-rich waters of the MR. The RR did not contribute directly to the enhancement of DIC loads, but rather had a dilutionary effect the MR's high DIC concentrations. However, by providing large loads of bioavailable DOC which can be rapidly mineralized to DIC, the RR may still have an indirect impact on end-member DIC export from the AR.

3.4.2 Dissolved Inorganic Carbon

Based on the relative abundance of C_3 and C_4 plants in the Mississippi River Basin (~72.7% and ~27.3%, respectively), Dubois et al. (2010) estimated that soil respired CO_2 in the MR basin should have an average isotopic signature of ~ -23.5‰. According to carbonate dissolution stoichiometry, the final $\delta\ ^{13}C_{DIC}$ value can be estimated as a 1:1 mixture of dissolved

carbonates, which typically have a value near 0‰ (Mook et al., 1983), and dissolved soil CO_2. Therefore, we would expect the average $\delta\ ^{13}C_{DIC}$ value in the lower Mississippi River to be half of the Dubois et al. reported soil CO_2, i.e. ~ -11.75‰, assuming an equal contribution of soil emission and carbonate dissolution. The average value found in this study, -12.0 ±0.9‰, agrees well with this expected value. This value is subject to enrichment by diffusion processes (+4.4‰ ; Cerling et al., 1991), as well as by gas transfer (+0.85‰; Zhang et al., 1995).

Using similar methodology, we can attempt to estimate an average expected isotopic value for the CO_2 Red River basin's soil, which heavily influences aquatic $\delta\ ^{13}C_{DIC}$. Nearly half of the vegetation in the RR basin is estimated to be made up by grasses (Matthews et. al, 2005), and between 60% and 70% of those grass species are estimated to use the C_4 photosynthetic pathway (Osborne et al., 2014). Assuming ~65% of grasses in the Red River Basin use a C_4 pathway, the relative abundance of C_3 and C_4 plants in the basin are ~67.5% and ~32.5%, respectively. Based on this, it can be roughly estimated that the Red River Basin soils have an average soil CO_2 isotopic value of ~ -22.8‰ and an average $\delta\ ^{13}C_{DIC}$ signature of ~ -11.4‰ in the river water. This value is different from the average value found in this study, -15.3 ± 1.9 ‰. The discrepancy between expected and reported values for the RR could indicate ^{13}C depletion of DIC via in-stream respiration in its warm waters, but more likely can be heavily attributed to climate conditions in the RR basin. The western grassland-dominated portion of the basin experiences arid, low precipitation conditions, while the temperate forested eastern region of the basin experiences higher rainfall. DOC is known to be exported at higher rates in accordance with rainfall and higher discharge (Wallace et al., 1995; Kiffney et al., 2000; Shen et al., 2012; Tian et al., 2015), so the majority of soil carbon in the RR may come from the C_3 dominant eastern region. Lowest $\delta\ ^{13}C_{DIC}$ values in the RR were observed in April 2016 (-18.4 ‰), when

the RR experienced a flood pulse (Figure 3.2). This agrees with evidence that most degraded materials are discharged during high flow periods (Cowie and Hedges, 1984; Ittekkot and Arain, 1986; Bianchi, 2004). Higher $\delta\ ^{13}C_{DIC}$ values which were observed during lower flow periods are then may indicate less degraded sources.

The more negative isotopic values of DIC in the RR are indicative of the dominance of natural soil emission typically observed in regions that are less degraded by anthropogenic alteration, whereas ^{12}C depleted values such as those found in the MR are characteristic of human-dominated watersheds with large agricultural and urban centers, where heightened DIC concentrations lead to increased weathering and atmospheric degassing (Iwata et al., 2013). These values may then illustrate important differences in the quality of dissolved carbon in these two rivers.

Highest $\delta\ ^{13}C_{DIC}$ values occurred in both rivers in September, which corresponded with highest concentrations of DIC in both rivers. CO_2 degassing can occur more rapidly when there is a greater difference between partial pressure of carbon dioxide in the air and in the water, as would be indicated by heightened DIC concentrations (Polsenaere and Abril, 2012). Calculated pCO_2 values based on reported DIC concentrations demonstrated that both tributaries to the AR were supersaturated with carbon dioxide in respect to the theoretical atmospheric value of ~390 ppm (Hartmann et al., 2013). Atmospheric degassing causes the preferential loss of the ^{12}C isotope, resulting in a carbon pool that is enriched in ^{13}C, which may provide explanation for the more positive $\delta\ ^{13}C_{DIC}$ values occurring in the MR (i.e., Geldern et al., 2014). However, seasonally, highest pCO_2 values (and thus highest rates of evasion) occurred in the winter and did not correspond with the increased values of $\delta\ ^{13}C_{DIC}$ in late summer and early fall months (Figure 3; Figure 5). Though degassing likely impacted DIC isotopic composition in both rivers,

it is clear that it was not the controlling factor. Since discharge was lowest when $\delta\ ^{13}C_{DIC}$ values were highest (Figure 2; Figure 5), riverine DIC may have been more strongly influenced by local soil weathering and groundwater, which are both relatively enriched in ^{13}C (Aufdenkampe et al., 2011; Johnson et al. 2008; Mayorga et al. 2005). Since the RR contributed ~46.5% of the AR's flow but only ~30.8% of daily DIC mass load on average, its impacts on isotopic values of the AR's waters are proportionally less than that of the MR. The $\delta\ ^{13}C_{DIC}$ signature of carbon exported to the NGOM can thus be expected to more closely resemble the less negative DIC isotopic values found in the MR.

3.4.3 Dissolved Organic Carbon

The AR's $\delta\ ^{13}C_{DOC}$ values, on the other hand, can be expected to be somewhat dominated by the significantly more negative signatures representative of the RR, since it contributed an estimated ~57.5% (± 24.4%) of the AR's daily DOC mass load on average. The MR and RR's relative influences on organic carbon isotopic signatures in the AR should then be closer to a 1:1 mixing ratio.

Sources and loads of DOC in the MR are controlled by inputs from the MR's upper tributaries (Kendall et al., 2001; Duan and Bianchi, 2006; Duan et al., 2007). As inputs of organic material travel downstream, they become degraded by in-stream processes so that DOC in the lower MR (and thus the AR) is less bioavailable, or, lower "quality" (Cole et al., 2007; Wipfli et al., 2007). However, since the RR travels a shorter distance through a less agriculturally-influenced region, it is probable that its DOC is fresher and less degraded. The significantly differing values of $\delta\ ^{13}C_{DOC}$ in the RR and MR could be indication of these potential differences in quality of organic material in the RR. The preferential use of atmospheric ^{12}C for

photosynthetic processes gives plant material a more negative signature – more negative δ $^{13}C_{DOC}$ signatures in the RR could then reflect higher concentrations of plant material or higher rates of in-stream primary production (Vuorio et al., 2006). Reliable interpretation of δ $^{13}C_{DOC}$ signatures is complicated by the overlapping signatures of major DOC sources (Schulte et al., 2011). It is difficult to constrain whether more negative signatures in the RR are due to in-stream production and young plant material inputs, or simply the distribution of C_3 plants in the basin, which would provide little indication of age or bioavailability.

Additional information on the quality of riverine organic matter can be obtained by determination of chlorophyll *a* (Holm-Hansen et al., 1965; Gregor and Marsalek, 2004) derived from pigmented plant material and algal production. Higher chlorophyll *a* content generally indicates younger and less degraded organic material, since chlorophyll *a* is rapidly degraded in the presence of light and oxygen, thereby becoming more depleted in older material (Moss, 1968). A 2010 study of the Red River basin found that the 25th percentiles of chl-*a* concentrations measured throughout the basin from 1996-2006 dramatically exceeded USEPA recommended values, particularly in the basin's largest ecoregions (Longing and Haggard, 2010). Though this present study did not analyze chl *a* concentrations, phycocyanin (a pigment found in cyanobacteria) fluorescence data was collected, and might serve as a general indicator of in-stream algal production. Significantly higher phycocyanin fluorescence measured in the RR compared to the MR over this study period (86.1 vs 61.9, $p = 0.046$, Table 3.2) could potentially indicate higher rates of in-stream production of organic material by the RR, thus providing a reactive and bioavailable source of DOC. Low ratios of DIC:DOC in the RR, generally below 1 (Figure 3.3), may also indicate the conversion of aqueous CO_2 to organic C by phytoplankton via in-stream primary production. The RR's heightened DOC concentrations depleted in ^{12}C found

during in this study, in conjunction with knowledge of high chl-*a* content, and evidence of potentially greater in-stream production rates, are probable indicators that the RR plays a significant role in delivering large quantities of bioavailable organic material to the Atchafalaya River.

While there was no relationship between $\delta\ ^{13}C_{DOC}$ and $\delta\ ^{13}C_{DIC}$ values in the MR (R^2 = 0.05, p = 0.50), there was a relatively strong negative relationship between $\delta\ ^{13}C_{DOC}$ and $\delta\ ^{13}C_{DIC}$ values in the RR (R^2 = 0.57, p < 0.01). This suggests that the sources and processing of DIC and DOC in the RR are closely interrelated. Coupling of DIC and DOC processing can occur when DIC is produced as a direct result of mineralization of DOC, or when DIC is taken up to produce organic material in stream (Cole et al., 2007). The relationship between $\delta\ ^{13}C_{DOC}$ and $\delta\ ^{13}C_{DIC}$ in the RR (and lack of relationship in the MR), in addition to the RR's low DIC:DOC ratios, and isotopic indication of less degraded DOC, all point to either fresh allocthonous inputs of DOC or in-stream production of organic material as a major contributor to the RR's high DOC loads. The results of this study indicate that bioavailable organic matter, regardless of whether it is allocthonous or autochthonous in origin, is an important factor in determining the DIC and DOC concentrations and quality in the Red River, and thus the Atchafalaya River.

3.5 Conclusions

This study provides insights into the isotopic composition of dissolved organic and inorganic carbon in the Red River, filling in a knowledge gap important to understanding carbon dynamics in large distributary river of the Mississippi. The isotopic values of both $\delta\ ^{13}C_{DIC}$ and $\delta\ ^{13}C_{DOC}$ in the RR were found to be significantly more depleted in ^{13}C than those of the MR. This, in conjunction with significant differences in DIC and DOC concentrations and mass loads,

demonstrates notable differences in the quality and quantity of carbon delivered to the AR by these two tributaries. The study suggests disproportionately high mass contributions of a younger, more bioavailable source of DOC to the AR via the RR, as well as an important dilution effect on the anthropogenically enhanced DIC flux from the diverted portion of the MR. The contribution of the Red River thus represents a significant component of dissolved carbon dynamics in the Atchafalaya River, and should be taken into account when developing carbon budgets for the NGOM. The RR likely plays an important role in determining end-member contributions of the AR to the Northern Gulf of Mexico, impacting estuarine and coastal processes, as well as CO_2 flux to the atmosphere.

CHAPTER 4: SUMMARY AND CONCLUSIONS

The quantity and quality of dissolved carbon delivered to coastal margins by rivers impacts estuarine and ocean biogeochemical cycling and ecological functioning, and is an important component of global carbon cycling. The Atchafalaya River (AR) flows 189 kilometers through the largest bottomland swamp in North America to discharge ~25% of the flow of the Mississippi River into the Gulf of Mexico annually, providing a unique opportunity to study floodplain impacts on dissolved carbon export in a large river system. This thesis research was conducted in order to: (1) determine DIC and DOC transport and processing by a river swamp basin under varied seasons and flow regimes, using the Atchafalaya River as a case study; (2) describe how the waters of the AR are compositionally affected, in terms of both quantity and quality of dissolved carbon constituents, by the relative chemical contributions of its major tributaries; (3) provide much-needed estimates for export of carbon to the NGOM by the AR. The primary goal of the research was to test the hypothesis that floodplain interactions in the Atchafalaya River Basin are related to enhanced opportunities for carbon cycling, resulting in net removal of dissolved organic material and production of inorganic carbon. These objectives were addressed through analysis of dissolved organic and inorganic concentrations, mass loads, and $\delta\ ^{13}C$ stable isotopic composition over a 13-month period spanning varied seasonal conditions and flow regimes. The data collected during this period represents the first comprehensive study of dissolved carbon in both the AR and the RR.

Dissolved carbon loads in the AR were found to be heavily impacted by the influence of the Red River, which differed significantly from the MR in terms of its chemical composition. DIC concentrations in the RR were found to be half of those found in the MR ($p < .0001$), while the RR's DOC concentrations consistently were double those found in the MR ($p < .0001$).

Based on the models developed for this study period, the RR's contribution to DIC mass loading in the AR represented 1.41 teragrams (Tg) (or, 29.7%) of the total 4.76 Tg DIC transported by both tributaries, while its contribution to DOC mass loading was disproportionately high, accounting for 1.74 Tg of the 2.75 Tg DOC (or, 63.2 % of total DOC) entering the AR. Both $\delta\ ^{13}C_{DIC}$ and $\delta\ ^{13}C_{DOC}$ showed significantly more negative values in the RR than were found in the MR, indicating differences in carbon sources and potentially quality. Significant correlation between $\delta\ ^{13}C_{DIC}$ and $\delta\ ^{13}C_{DOC}$ isotope values in the RR indicated interrelation of dissolved carbon sources or processing, which was not observable in the MR. Significant differences in DIC and DOC concentrations, isotopic composition, and mass loads in the MR and RR must be accounted for in studies of carbon in the AR. This study suggests disproportionately high mass contributions of a younger, more bioavailable source of DOC to the AR via the RR, as well as an important dilution effect on the anthropogenically enhanced DIC fluxes from the diverted portion of the MR. The flow contributions of the Red River thus represent a significant component of dissolved carbon dynamics in the Atchafalaya River, and should be taken into account when developing carbon budgets for the NGOM. The RR likely plays an important role in determining end-member contributions of the AR to the Northern Gulf of Mexico, impacting estuarine and coastal processes, as well as CO_2 flux to the atmosphere.

DIC concentrations in the AR were found to be 3 times higher than DOC concentrations on average, and showed more pronounced downstream changes than DOC. During the study period, the AR delivered a total of 5.35 Tg DIC and a total of 2.34 Tg DOC into the Gulf of Mexico. Based on the mass inflow-outflow balance, approximately 0.53 Tg (~10%) of the total DIC exported was produced within the floodplain, while 0.24 Tg (~ 10%) of DOC entering the basin was removed. The AR was consistently saturated with CO_2 above atmospheric CO_2

pressure (with pCO_2 varying from 551 µatm to 6,922 µatm), indicating a large source of DIC from river waters to the atmosphere as well as to coastal margins. This demonstrates that a large river with extensive floodplains in its coastal margin can act as a significant source of dissolved inorganic carbon both to coastal systems and to the atmosphere, and may also be important sinks for dissolved organic carbon. This effect was particularly pronounced during higher-than-average flow periods where extensive interactions between river and floodplain soils and backwaters are able to take place, especially during initial flood stages. The influence of floodplain interactions on biogeochemical cycling of carbon in this system may be due to a net heterotrophic response to high productivity within this large subtropical river swamp system, with high CO_2 inputs stemming from respiration in floodplain soils, vascular plant root zones, and in the water column. This is indicated by trends in dissolved carbon concentrations, mass loads, and isotopic composition from inlet to outlet locations, as well as seasonal trends in pCO_2 and DIC:DOC throughout the study period.

This study was conducted during an abnormally wet summer and winter, which resulted in very high flow and high mass exports of dissolved organic and inorganic carbon into the Northern Gulf of Mexico. These results are of particular interest as we continue to evaluate changes in riverine carbon transport and processing in light of our rapidly changing climate. As discharge of many of the world's rivers are projected to increase in coming years due to global warming and intensified hydrological cycling, increased carbon fluxes to coastal zones should be anticipated. Low-lying floodplain systems such as the studied Atchafalaya River must be taken into account when examining modern carbon budgets, and may need to be looked to in future years for the filtration and removal of organic materials, which impact coastal margins and ocean ecosystems as a whole.

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